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Research Article

Effect of Calcination Temperature on the Perovskite Characteristics Prepared by Modified Pechini Method

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Abstract

Perovskite type oxides which have the general formula as ABO_3 including both rare earth elements and 3d transition metals is gaining interest according to be utilized as such strategic materials because of their excellent catalytic, magnetic, electrical and optical properties. Along with perovskitic materials, lanthanum nickel oxide ($LaNiO_3$-LNO) shows potential as a consequence of its electronic and catalytic properties in not only reactions like reforming, redox reactions but also in storage and conversion of energy or synthesis an electrode material. LNOs are widely prepared by methods like sol-gel, co-precipitation, solid state and Pechini. Among these methods, the Pechini method practices the metal salts consisting of nitrates, acetates, etc. as precursors and citric acid (CA) as a chelating agent of metal ions and ethylene glycol (EG) utilized like a cross-linking agent to arrange a polymeric resin based on molecular level and declines metal ions segregation and confirms compositional homogeneity. This process can defeat most of the difficulties and disadvantages that frequently occur in the alkoxides related to sol−gel method. The study attempts to scan the influence of calcination temperature on the physical properties of $LaNiO_3$ catalysts prepared by modified Pechini method without ethylene glycol. In order to lay out the physical properties, X-ray diffraction (XRD), scanning energy micoscopy (SEM), and N_2 adsorption/desorption techniques were used. The change with the temperature in the structure caused a decline in specific surface area, pore volume and rise in pore size. XRD results showed that LNO calcinated at 700°C favored the establishment of an almost homogeneous $LaNiO_3$ phase rather than calcination at 500°C. The study underlined that the preparation of the LNO by the modified Pechini method can be applied successfully with the temperature above 700°C without EG as a cross-linking agent.

Keywords: Perovskite, Calcination Temperature, $LaNiO_3$, Modified Pechini method.

Kalsinasyon Sıcaklığının Modifiye Edilmiş Pechini Yöntemi ile Hazırlanan Perovskit Özelliklerine Etkisi

Öz

Hem nadir toprak elementlerini hem de 3d geçiş metallerini içeren ABO_3 genel formülüne sahip olan Perovskit tipi oksitler, mükemmel katalitik, manyetik, elektrik ve optik özelliklerinden kaynaklanan stratejik malzemeler olarak kullanılmalarından dolayı oldukça dikkat çekmektedir. Perovskitik malzemeler arasında lantan nikel oksit ($LaNiO_3$-LNO), yalnızca reform ve redoks gibi reaksiyonlarda değil, aynı zamanda da enerji dönüşümü veya elektrot malzeme sentezinde önemli bir potansiyele sahiptir. LNO'lar yaygın olarak sol-gel, birlikte çöktürme, katı hal ve Pechini gibi yöntemlerle hazırlanır. Bu metotlar arasında Pechini yönteminde öncü maddeleler olarak yaygın olarak kullanılan nitratlar, asetatlar, klorürler, vb. ve şelatlama ajanı olarak sitrik asit (CA) ve çapraz

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bağlayıcı olarak moleküler seviyede bir polimerik reçine oluşturması, metal iyonlarının ayrışmasını azaltması ve yapıda homojenliği sağlaması sebebiyle etilen glikol (EG) kullanır. Pechini yöntemi ile alkoksit bazlı sol-jel yönteminde sıklıkla ortaya çıkan zorlukların ve dezavantajların birçoğunun üstesinden gelmek mümkün görünmektedir. Bu çalışma ile kalsinasyon sıcaklığının, etilen glikol içermemek sureti ile modifiye edilmiş Pechini yöntemi ile hazırlanan $LaNiO_3$ katalizörlerinin fiziksel özellikleri üzerindeki etkisini detaylı bir şekilde ortaya koymaktadır. Fiziksel özelliklerin incelenmesi amacıyla, X-ışını kırınımı (XRD), Taramalı elektron mikroskopisi (SEM) ve N_2 adsorpsiyon/desorpsiyon teknikleri kullanılmıştır. Sıcaklıktaki değişime bağlı olarak LNO perovskit yapıda yüzey alanında azalma ve gözenek hacmi ve gözenek boyutunda artış gözlenmiştir. XRD çalışmaları ile 700°C'de kalsine edilen LNO perovskit tipi oksitinin, 500°C'de kalsine edilen perovskit ile kıyaslandığında neredeyse homojen bir $LaNiO_3$ perovskite fazı oluşumu sağladığı ortaya konmuştur. Çalışma, LNO'nun çapraz bağlama maddesi olarak EG içermemek sureti ile modifiye edilmiş Pechini yöntemi ile 700°C'nin üzerindeki kalsinasyon sıcaklıklarında çalışılması durumunda başarıyla hazırlanabileceğinin altını çizmektedir.

Anahtar Kelimeler: Perovskit, Kalsinasyon sıcaklığı, $LaNiO_3$, Modifiye edilmiş Pechini yöntemi.

1. Introduction

Perovskites denoted by the general formula ABO_3 (where: A is a rare earth element; B is a transition metal) are getting awareness in the past two decades due to the possibilites for utilizing as fuel cell anodes and cathodes, catalysts, photocatalysts and thermoelectric materials (Granger et al., 2015). Numerous metal cations are established in the assembly of perovskite ABO_3, approved that their cationic radii show the size of 12-coordinated A and 6-coordinated B sites: $r_A > 0.90$ Å and $r_B > 0.51$ Å.

Perovskites can be synthesized using many methods like sol-gel, hydrothermal, spray pyrolysis, co-precipitation, solid state and Pechini. The properties of perovskites count on the method of manufacturing them. The dimension of perovskite particles strongly influences their structural and magnetic properties (Kucharczyk et al., 2019). Sol-gel method is almost certainly one of the most fundamental, practical and routine methods which has been used, developed and modified in researches for many years (Barakel and Ghorbel, 1998). Within years, a method of polymeric precursors established via Pechini by modifying sol-gel method (Barros et al., 2006). While the particles exists a gel structure in sol-gel method, the metal cations are surrounded in the polymer gel in the Pechini method. This diminishes the capability to develop controlled natures and includes the development of hard crystallite agglomerates. The dimension of the concluding creation is well-ordered, to an extent, by the sintering procedure and the early concentration of metals exist in the gel (Dimesso, 2018).

The Pechini process suggests numerous benefits over other methods, as well as low price, respectable compositional homogeneity, great purity, and comparatively low treating temperatures (Agarwal & Liu, 1997). Likewise, the Pechini process was utilised for the production of electric and magnetic materials rather comprehensively, as well as ferroelectric and capacitors, superconducting materials, photocatalytics, magneto-optical materials, and electrolytics in order to utilize in solid oxide fuel cells (Dimesso, 2018). However, the drawback of the Pechini technique, similar to many techniques, is positioned in the absence of size and morphological control.

The method is founded on the metallic citrate polymerization exhausting ethylene glycol. In general, citric acid (CA) is utilized as chelate cation (Lopes et al., 2009). Citrate has the capability to figure out complex structures and chemical homogeneity concluded mixing at molecular level in the solution with a fixed control of the stoichiometry (Niranjan et al., 2005). The accumulation of a glycol favors to the development of an ester. Polymerization is expected to promote by heating of the mixture (Lopes et al., 2009). Ammonium hydroxide is also utilized as adjusting the pH and to prevent lead citrate precipitation (Lemos et al., 2005).

In the literature, it is possible to find studies underlying the effect of hydrocarboxylic acid and glycols in Pechini method. The researchers investigated alternative routes without chelating or cross-linking agents. For instance, Selbach et al. studied about developing an adapted Pechini technique where citric acid was substituted with malic, tartaric acid and maleic acid were utilised for procurement $BiFeO_3$ powders and lead to singl phase $BiFeO_3$ from 425 to 500°C. In case of using malic acid instead of citric acid without EG, it was able to achieve single $BiFeO_3$ phase. When the researchers used tartaric acid without EG, $Bi_2Fe_4O_9$ was observed as a second phase beside $BiFeO_3$ phase (Selbach et al., 2007). Besides, Wang et. al studied about molybdenum oxide (MoO_2) microspheres by adapted Pechini technique. The effects of CA, EG, and H_2SO_4 existence on the development of MoO_2 examined in detail. Their outcomes verified that EG is advantageous for the spherical morphology (Wang et al., 2006).

To the best of found knowledge, there are few studies which include Selbach et al. and Wang et al. that deal with especially synthesis of perovskite without ethylene glycol via Pechini's method. Within this framework, the current work targets to search the influence of calcination temperature on the structural of the perovskite in detail. Accoring to this, the samples were arranged by modified Pechini technique and calcined at 500, and 700°C was characterized by XRD, S_{BET} analysis and SEM. The effect of calcination temperature with modified Pechini method is deliberated in the light of such information.

2. Material and Method

A modified Pechini technique was used to arrange the samples. Powders of $La(NO_3).6H_2O$ (from ABCR, 99% purity) and $Ni(NO_3)_2.6H_2O$ (from Panreac, 99% purity) were evaluated according to the calculated quantities and dissolved in distilled water. Citric acid (from ADR, for synthesis) was used as a chelating agent. The solution was heated at 90°C fixed for 10 hour (Rida et al., 2012). The final powder was calcined at 500°C or 700°C for fixed 5 hour. While sample calcinated at 500°C was denoted as LN5, the sample obtained at 700°C ascribed as LN7.

The crystalline and phase identification of the LNOs was achieved via PANalytical X'Pert Pro Materials Research Diffractometer using CuKα radiation (λ=0.15406 nm). The X-ray tube was functioned at 45 kV and 40 mA with a step size of 2°/min from 10 to 90° (2Θ). The textural properties including Brunauer–Emmett–Teller (BET) specific area, pore volume and average pore diameter (Barrett-Joyner-Halenda (BJH) method) were achieved from nitrogen physisorption capacities at a relative pressure of P/P_o =0.98 using a Micromeritics ASAP 2020 instrument. The morphology of catalysts was studied using a Zeiss Supra VP 40 scanning electron microscope with SE2 detector operating at 15 kV.

3. Results and Discussion

The XRD measurements carried out on the LNO catalysts are illustrated in Figure 1. LNO catalyst calcined at 700°C showed that the structure consisted of hexagonal LaNiO3 (Ref. Code: 98-017-3477) and a small amount of hexagonal NiO (Ref. Code: 98-016-6115) phases at 2Θ = 37.8 and 43.6 diffractions. Ortorombik La_2NiO_4 (Ref. Code: 98-000-0244) phase was detected besides hexagonal NiO and hexagonal La_2O_3 (Ref. Code: 98-002-6864) phases in LN5. The structure of La_2NiO_4 belongs to the perovskite structure of A_2BO_4. One of the previous studies showed that it is possible to meet this structure due to the insufficient calcination temperature (Guo et al., 2003). The XRD peaks of the LNO samples showed that along with the rise of calcination temperature, the peak intensity enlarged.

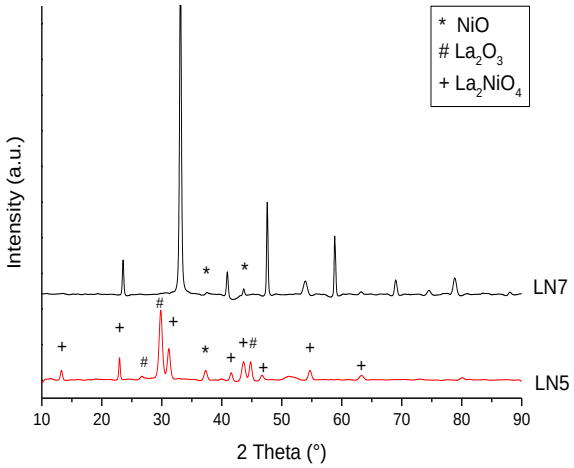

Figure 1. XRD spectrum of LNO samples.

The SEM micrographs of LNOs structures (Figure 2) indicated that samples were aggregated with irregular shapes for LN7. The surfaces of the layer in LN7 were wrinkled. Small particles formed in the big agglomerates were noticed with increasing the calcinations from 500 to 700°C. LN5 was more porous and collected of numerous tiny spots which also can be expected from higher BET surface area result as well.

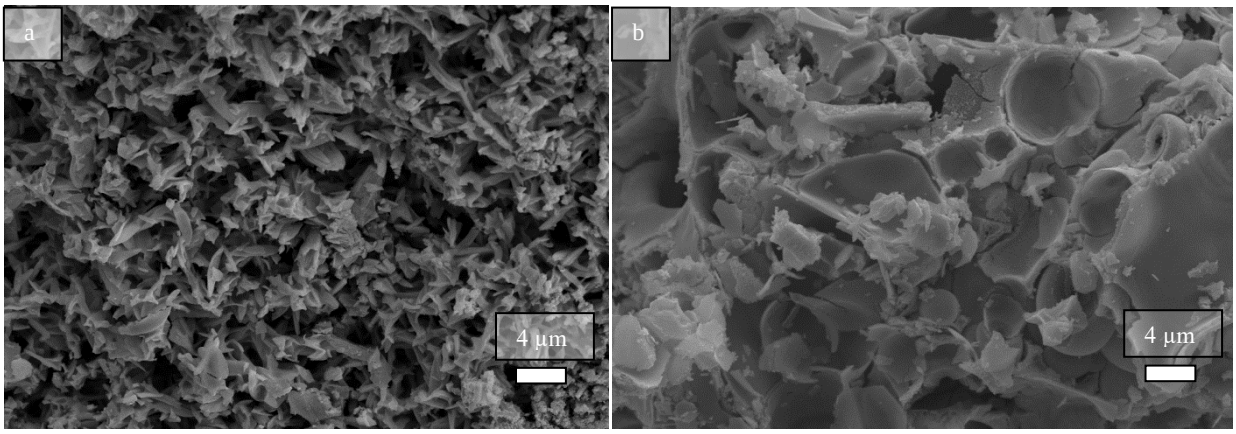

Figure 2. SEM images of: (a) LN5 and (b) LN7.

The textural properties including surface area, pore volume and average pore diameter is given in Table 1. The change with the temperature in the structure caused a reduction in surface area, pore volume and growth in pore size. This suggests that some of LNO species are incorporated which is consistent with SEM results. The structural parameters obtained indicated that the LNO species

could be successfully incorporated into the pores when the calcination temperature increased as can be seen from the decreasing BET surface area value clearly. According to the IUPAC Classification, adsorption-desorption isotherms given in Fig. 3. corresponded type III with an H3 hysteresis loop.

For pore size evaluation, the equation of Harkins and Jura was utilised (Fidalgo et al., 2013). The pore size distribution in terms of Harkins and Jura plot with FAAS correction were given in Fig. 6. The pores in structures of perovskites were uniformly distributed. Wide pore size distributions were as observed, ranging from 2-90 nm for LN5 and 14-80 nm for LN7.

Table 1. Textural properties of the catalysts.

Sample	S_{BET} (m^2/g)	Vp (cm^3/g)	Dp (nm)
LN5	15.2	0.04	9.80
LN7	4.86	0.03	31.9

S_{BET}: BET surface area; VP: Total pore volume; DP: Pore diameter.

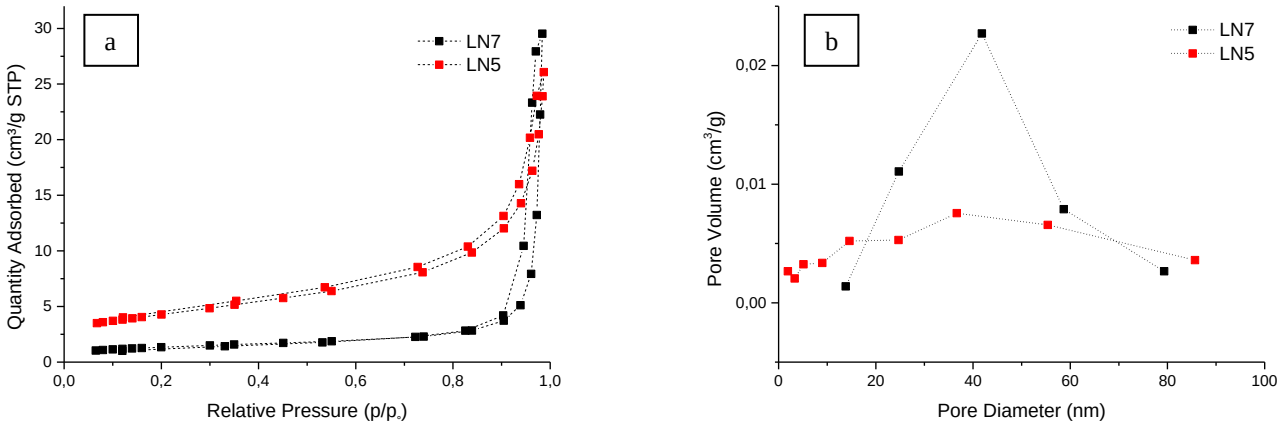

Figure 3.a)N_2 adsorption/desorption isotherms and b)pore size distributions of LNOs.

4. Conclusion

A modified Pechini method for preparing $LaNiO_3$ fine powders was applied. By using BET, XRD and SEM techniques, the influence of the calcination temperature on phase transformation and particle size of perovskite was studied in detail. The calcination temperature has been established to have a noticeable effect on the development of LNO and its particle size. The La_2NiO_4 perovskite phase with equisized, spherical and well-dispersed particles was detected at low temperature whereas almost single acceptable $LaNiO_3$ phase with clusters and agglomerates rather than uniform spheres were found at high temperature. The increase in calcination temperature caused a reduction in the BET specific surface area besides average pore size was increased. At the same time this clues to a rise in the degree of crystallization and result to an almost single phase perovskite which shows that the BET results were in consistent with SEM results. According to the results, single perovskite phase can be accomplished via Pechini method without ethylene glycol in case of calcination temperature above 700°C.

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