

Effects of the Solvent and Calcination Temperature on LaFeO₃ Catalysts for Methanol Oxidation

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ABSTRACT: *In this work, two types of solvents ethanol or water were used in preparation of the LaFeO₃ catalysts by citrate sol gel method. The obtained samples were subjected to various calcination temperatures in order to study the catalytic activity and stability for methanol electro-oxidation by XRD, cyclic voltammetry and chronoamperometry. The crystallinity of the LaFeO₃ phase in both cases is improved with increasing calcination temperature. The samples prepared using ethanol exhibit higher catalytic properties than those prepared in water for different calcination temperatures. Moreover, the catalyst prepared in ethanol and calcined at 1050 °C, exhibits a high catalytic activity in methanol electro-oxidation and is ~ two times greater than that obtained at 750 °C.*

KEYWORDS: *LaFeO₃; Solvent effect ; Calcination temperature ; Methanol oxidation.*

INTRODUCTION

Many efforts are actually focused on the search for low cost materials with high electro-activity mainly in order to produce a suitable replacement for the traditional precious metal catalysts [1]. LaMO₃ (M = Co, Fe, Mn) perovskite oxides have shown an adequate catalytic activity towards a number of oxidation reactions, hexane [2], benzene[3] and CH₃OH [4]. Among these promising catalysts, perovskite-type oxide LaFeO₃ which has shown gas sensing properties, especially for toxic and noxious gases of NO₂ and CO [5]. Also, It has been the object of many studies in order to lower the preparation temperature and to obtain an ultrafine and chemically pure powder [6-9]. Indeed, it was reported that catalytic performances of perovskite oxides depend on both homogeneity and calcination temperature. *Kahoul et al.* reported that the use of propanol as a solvent

of the precursors leads systematically to the formation of homogeneous La_{1-x}Ca_xCoO₃ oxides with a single perovskite structure phase, larger surface area, and higher conductivity values compared with those prepared using water [10]. On the other hand, the effect of calcination temperature on the methane partial oxidation over perovskite-type LaFeO₃ oxide was investigated [11]. This study shows that the CO selectivity remained at a high level of 92%, and increased slightly as the calcination temperature increased. To our best knowledge, there is no study on the effect of the nature of solvent and the calcination temperature on the methanol oxidation over perovskite-type LaFeO₃ oxide. From these points of view, in this work, LaFeO₃ oxides prepared by the citrate sol gel method using two solvents ethanol and water are calcined at 400 ≤ T ≤ 1050°C. Cyclic voltammetry and

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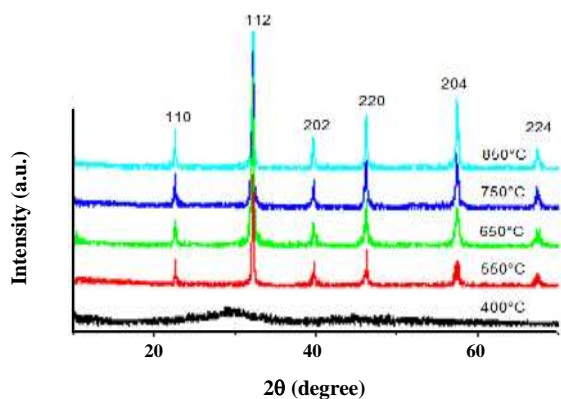


Fig. 1: XRD patterns of the powders LaFeO_3 calcined at different temperatures (W).

chronoamperometry studies are conducted on the two prepared series denoted (W), (E) for water and ethanol respectively, in order to evaluate the effect of the nature of the solvent and the calcinations temperature on their catalytic activities for methanol oxidation.

EXPERIMENTAL SECTION

Lanthanum ferrite was synthesized by the citric acid sol-gel method. Aqueous solutions of $\text{La}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Biochem), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Biochem) were first dissolved in absolute ethanol or water separately. Citric acid (Biochem) was added to the precursors under vigorous stirring. The obtained solution was heated at 110°C for 12 h and calcined from 400 to 1050°C under air to obtain the final powder.

XRD characterization of samples was carried out with a D8 Advance-Brucker using a $\text{Cu K } \alpha$ line at 0.1540 nm. The electrochemical experiments for O_2 reduction and evolution were performed using a Volta Lab 40 potentiostat/galvanostat. The measurements were carried out in a three-compartment cell. Potassium hydroxide electrolyte was prepared by dissolving the required amount of KOH (Merck) into bidistilled water. The working electrodes (1cm^2) were obtained by painting, with an oxide suspension. The loading of catalyst films was $12 \pm 3 \text{ mg/cm}^2$ in each case. The counter electrode used was a Pt plate. The reference electrode was $\text{Hg/HgO}/ 1\text{M KOH}$. All potentials in the text have been referred to this reference electrode. The voltammetry experiments were performed in 1M KOH solution containing 1M CH_3OH at scan rates of 5, 10, 20, 50, 100 mV/s. The chronoamperometry (current versus time response) tests

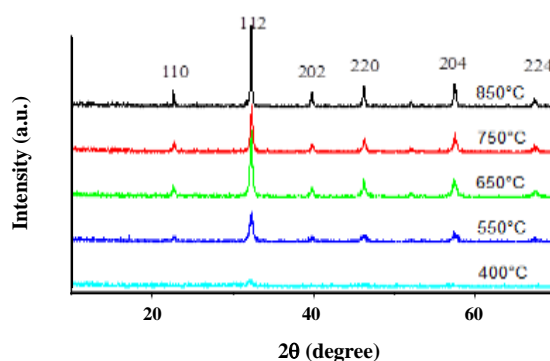


Fig. 2: XRD patterns of the powders LaFeO_3 calcined at different temperatures (E).

were conducted using a three-electrode cell in 1M KOH solution containing 1 M CH_3OH at 0.5 V for the period of 30 mn.

RESULTS AND DISCUSSION

X-ray diffraction

Figs. 1, 2 present XRD patterns of (W) and (E) LaFeO_3 series respectively. In both cases, After being heated at 400°C in air, the powder is almost amorphous. When the powder is calcined at $T \geq 550^\circ\text{C}$, the amorphous phase disappears and the characteristic peaks of the perovskite phase appear with low intensity, which signified the transformation of amorphous phase to the crystalline pure orthorhombic phase. The crystallinity of the LaFeO_3 phase is improved with increasing calcinations temperature. By comparing at the same temperature the patterns of the two series, we observe clearly that peaks of samples serie (E) are higher than those of serie (W). Further heating only increased the intensity of the X-ray peaks and no other phase peaks are observed.

The same result was also reported using a bio-inspired method [12] and another based on the thermal decomposition of a cyanide-bridged heteronuclear complex $\text{La}[\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ [6], indicating that LaFeO_3 begins to crystallize into the pure orthorhombic structure at 600°C and its crystallinity increases with increasing calcinations temperature. While using the co-precipitation method [6], XRD patterns at different temperatures indicate that the perovskite phase becomes pure at the calcining temperature above 800°C .

The peak broadening at lower angle is more meaningful for the calculation of particle size therefore

size of nanocrystals has been calculated using Debye-Scherrer formula [13]. This formula for crystallite size determination is given by:

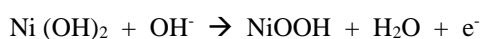
$$D = 0.89 \lambda / \beta \cos \theta \quad (1)$$

Where D is the crystallite size, λ is the wavelength of x-ray, β is the full width at half maximum (β expressed in radians), θ is the Bragg's angle. The crystallite size obtained from XRD for different calcination temperatures is presented in Fig. 3. In both cases, it is clear that the crystallite size increases with increasing temperature and it is substantial after heating to above 750°C. In fact, it increases from 19 to 46 nm (serie E) and from 25 to 50 nm (serie W) in the calcination temperature range 550-850°C. It was attributed to a typical effect of temperature on crystal growth. The same trend was also found for LaFeO₃ prepared by a sol gel method using glycine as a chelating agent [11]. The obtained crystallite size of serie (E) samples are smaller than those of serie (W). The same result was also found by Jie *et al.* [14]. It has been shown that the powder dispersion is better using the solvent absolute alcohol than water. It is verified that absolute alcohol as solvent can reduce capillarity remarkably and prevent original particles from reuniting.

Electrochemical Properties

Effect of scan rate on electrochemical behavior of LaFeO₃ oxides

Figs. 4 and 5 present the voltammograms of LaFeO₃ oxide at five scan rates calcined at 950 °C for series (W) and (E) respectively. We find in general that this electrode has a qualitatively similar behavior for the two series. The voltammograms at scan rate of 5, 10, 20, 50 and 100 mV/s exhibit two anodic peaks in both anodic and cathodic sweeps, prior to the onset of the O₂ evolution reaction corresponding to the electro-oxidation of methanol. At the more cathodic potential side, in all cases a weak reduction peak appeared. This peak is probably due to the couple Ni (II) / Ni (III) from the nickel substrate [15] according to the reaction:



In the anodic sweep, the anodic peak appears at around 0.60 V as shown in Figs. 4, 5. After peak formation, the oxygen evolution begins. Whereas, in the cathodic sweep, the oxidation of methanol recommences

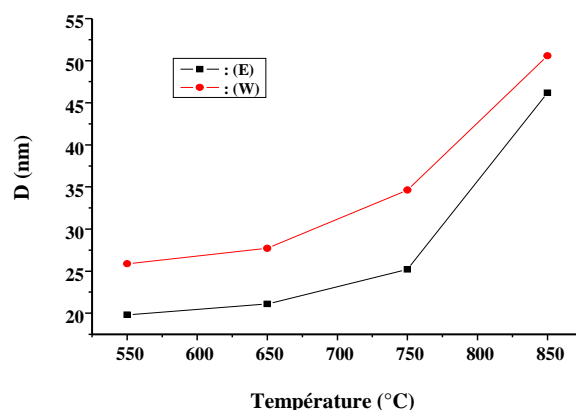


Fig. 3: Crystallite size D of (W) and (E) LaFeO₃ series calcined at different temperatures.

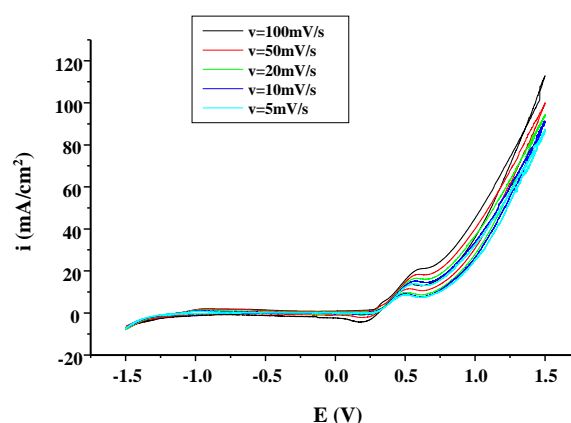


Fig. 4: Cyclic voltammograms of LaFeO₃ (W) catalyst calcined at 950°C in 0.1 M KOH + 0.1 M CH₃OH.

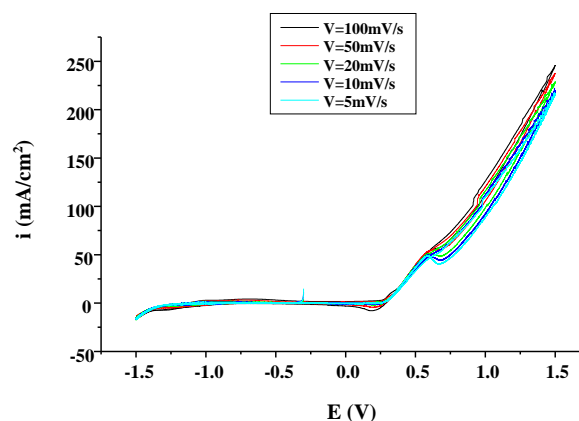


Fig. 5: Cyclic voltammograms of LaFeO₃ catalyst (E) calcined at 950°C in 1 M KOH + 1 M CH₃OH.

at lower potential and gave a small reverse anodic peak at ~ 0.52 V.

These figures show also that in both cases, the peak current for the electro-oxidation of methanol increased with increasing scan rates. The peak current varies approximately linearly with square root of scan rate (Fig. 6). This result appears in favor of the fact that the process of electro-oxidation of methanol has the characteristics of a diffusion-controlled process [16].

With the increasing of the scan rate both anodic and cathodic current increases and the cathodic peak potentials have shifted towards negative values, while anodic peak potentials move to more positive values. This observation suggests also that the electrode process is diffusion controlled. The peak potential of the anodic peaks of cyclic voltammograms of the electro-oxidation of methanol shifted toward more anodic potential with increasing scan rate. This is a characteristic property of quasi-reversible or an irreversible electrode reaction [17].

Electro-catalytic activity of LaFeO_3 oxides

Figs. 7 and 8 show the polarization curves for the electro-oxidation of methanol (1M CH_3OH + 1M KOH) over LaFeO_3 samples series (W) and (E) respectively. The measurements were conducted using a potential scan rate of 20 mV/s. From these figures, it can be seen that the current of the methanol oxidation becomes apparent as the potential rises above 250 mV.

The catalysts LF_{1050} exhibit higher catalytic activity toward the methanol oxidation in both cases with onset potentials both around 0.27 (E) and 0.3 V (W). This result indicates clearly the effect of calcinations temperature on the catalytic activity of these oxides on methanol oxidation. This is in good agreement with anterior results on methanol oxidation over $\text{La}_{0.8}\text{Sr}_{0.2}\text{MO}_3$ ($M = \text{Co}, \text{Mn}$) [18]. It has been shown that increasing of calcinations temperature produces a decrease of the specific surface on one hand and an improvement of the catalytic activity per unit area reduced for the oxidation of methanol on the other hand. The catalytic performance of the LaFeO_3 sample is relevant with the crystalline size and the rate of oxygen migration from bulk toward surface [11]. The effect of calcination temperature on the catalytic activity is probably due to the increase of oxygen vacancies generated with increasing temperature, which are essential to allow the adsorption of methanol.

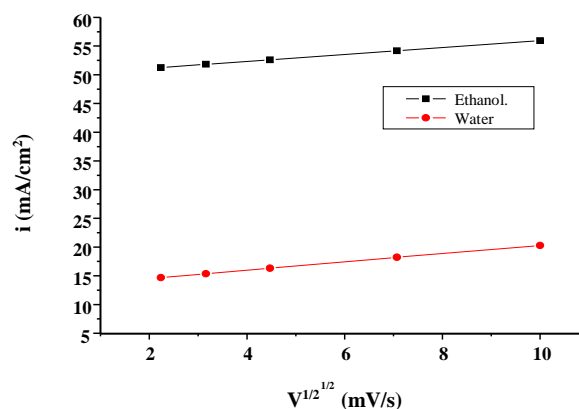


Fig. 6: Anodic current density of LaFeO_3 as a function of a square root of the scan rate.

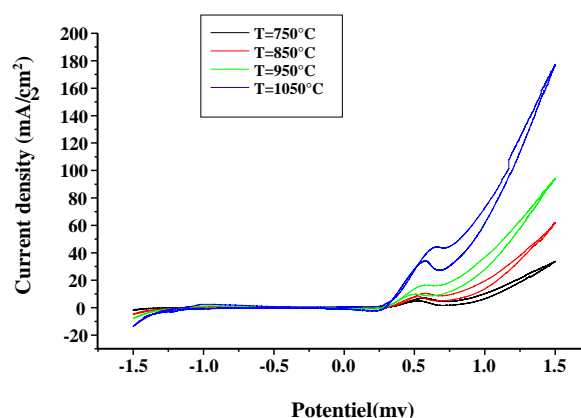


Fig. 7: Cyclic voltammograms of LaFeO_3 (W) catalyst calcined at 950°C in 1 M KOH + 1 M CH_3OH at different temperatures. scan rate = 20 mV/s

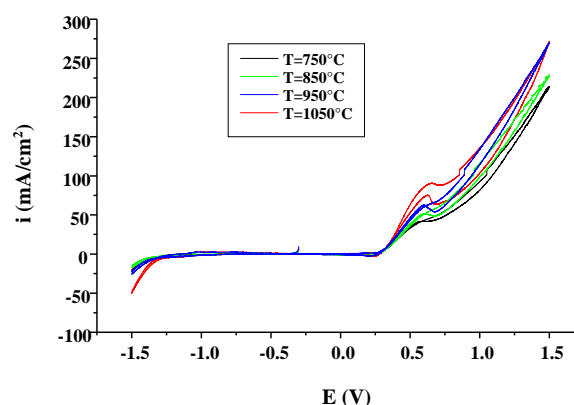


Fig. 8: Cyclic voltammograms of LaFeO_3 (E) catalyst calcined at 950°C in 1 M KOH + 1 M CH_3OH at different temperatures. scan rate = 20 mV/s.

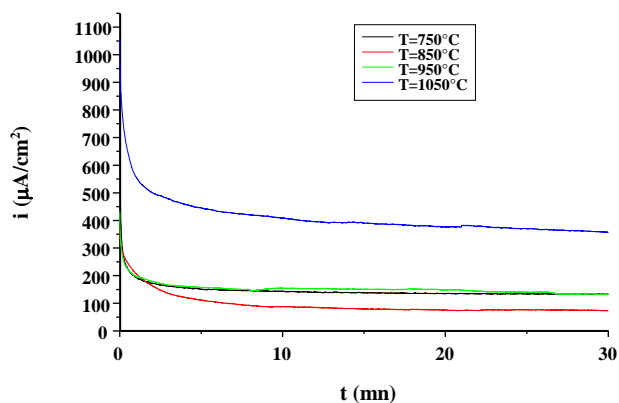


Fig. 9: Chronoamperometry curves of methanol oxidation on LaFeO₃ catalyst (W) at 500 mV.

This is in good agreement with measured Seebeck coefficients of LaFeO₃ upon heating indicates the increase in the positive values that can be ascribed to the increase in the concentration of positively charged oxygen vacancies generated intrinsically [19]. *Levasseur et al.* [4] have studied the methanol oxidation on LaBO₃ (B=Co, Mn, Fe) catalysts prepared by reactive grinding. It has been shown the temperature dependence of oxygen vacancies in LaBO₃ oxide. In fact, TPD-O₂ experiments show two types of desorbed oxygen species: the one coming from the surface (α -oxygen) at $T < 750^\circ\text{C}$ and the other from the bulk (β -oxygen) at $T > 750^\circ\text{C}$, thus leading to the creation of anionic vacancies. This trend was also confirmed by conductivity measurements [20]. It was reported that the conductivity increases with increasing the calcination temperature for LaFeO₃ oxide. The catalytic activity of the catalyst prepared with ethanol is greater than that prepared with water for each calcination temperature. This indicates clearly that the parameter solvent plays an important role on these catalysts. In fact, the catalyst dispersion was inversely proportional to viscosity of the solvent [21]. The same behavior was also found in the preparation of La_{1-x}Ca_xCoO₃ catalysts using propanol and water as solvents in the starting solution [10]. It was reported that propanol solvent seems more effective than water in producing an amorphous precursor yielding oxides with finer grains. The obtained fine powder using solvent ethanol yields to a better catalytic property of these catalysts. This is in good agreement with previously works [10, 21]. Which show clearly the dependence of the solvent nature

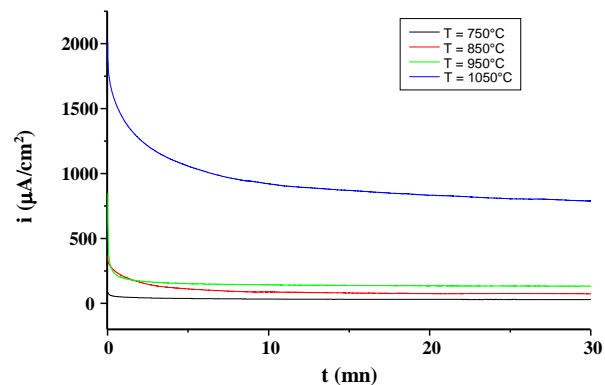


Fig. 10: Chronoamperometry curves of methanol oxidation on LaFeO₃ catalyst (E) at 500 mV.

to catalytic activity of catalysts. In fact smaller grain size brings a larger specific surface area and a higher surface activity, and therefore the activation energy of the surface adsorption and reaction will be reduced [22]. These results indicate that the calcination temperature and the solvent nature seem to play a key role in the preparation of catalysts for methanol oxidation.

Chronoamperometric study

The stability of LaFeO₃ electrodes for methanol oxidation was investigated by chronoamperometric measurements. Figs. 9, 10 show chronoamperometric curves of methanol oxidation on LaFeO₃ oxides series (W) and (E) at a potential of 500 mV respectively. The best results were observed for the electrode with the high calcination temperature for the two series. By comparison the catalyst LF₁₀₅₀ prepared using ethanol solvent exhibits the higher current value confirming the results obtained by cyclic voltammetry.

Analyzing Fig. 10, it is observed that the current density after 30 min is about 800 μAcm^{-2} for the LF₁₀₅₀ (E), which is $\sim 200\%$ higher than the current density for methanol oxidation on LF₁₀₅₀ (W) at the same potential. Then, it is evidenced that the higher calcination temperature and the solvent nature present an enhanced electrocatalytic performance because of the formation of nanoparticles with small size and the increase of oxygen vacancies. With the results exposed above the best electrocatalytic performance for methanol oxidation was for LF₁₀₅₀ (E). The explanation for this behavior can be associated to a synergic effect of

calcinations temperature and the solvent nature in the starting solutions.

CONCLUSIONS

In this work, LaFeO₃ nanoparticles were prepared using ethanol and water as solvents in starting solutions and calcined in the temperature range 750-1050 °C, characterized for methanol oxidation reaction. It was observed that the catalyst calcined at higher temperature and prepared using ethanol as solvent promotes the highest enhancement in the electrocatalytic performance for methanol oxidation. The observed phenomenon is associated with a synergic effect of LaFeO₃ nanoparticles and calcination temperature, where different reasons for this should be pointed out: (i) the solvent ethanol yields to a better dispersion of the powder with finer grains size, (ii) the higher calcination temperature generates more oxygen vacancies which are essential to allow the adsorption of methanol.

These two associated factors yield to a high surface adsorption and therefore the activation energy of the surface adsorption and reaction of methanol oxidation will be reduced.

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