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Original Research Article

Ambient-Stable $CaFeO_4$ Synthesis Process wet

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Abstract

The aim of this work is to prepare the room-stable calcium ferrate $CaFeO_4$ from Na_2FeO_4 chemically synthesized from ferric salts, in an alkali hydroxide medium and hypochlorite which is a particularly effective oxidizing agent in the synthesis, respecting the filtration, purification and drying processes required for the synthesis, because each change can lead to decomposition and decrease in purity. The calcium ferrate synthesis process consists in substituting the sodium ions of the VI ferrate obtained by Calcium by mixing them with a solution of calcium nitrate $Ca(NO_3)_2$, in order to study and optimize the essential parameters influencing the yield substitution as well as monitoring of its degradation over time, the reaction yield of which is of the order of 98.7% at a temperature of around [0 ° C - 40 ° C] and of pH = 11 for 30 minutes. The phase obtained was characterized by UV spectrophotometer by measuring the optical density at a wavelength of 507 nm and by the volumetric titration method.

Keywords: Ferrate, oxidant, electrochemical, cathode, Calcium ferrate (VI), Purity, Stability.

INTRODUCTION

The development of iron (VI) synthesis processes is proving to be very delicate, due to the oxidizing power of iron (VI). Among all the oxidants / disinfectants, practically used for the treatment of water and pollutants in water [1].

Ferrates are in high demand because it has a standard potential of FeO_4^{2-} / Fe^{3+} = 2.2 V, the evolution of water pollution presents very dangerous statistics thanks to the appearance of new pollutants.

Although the existence of alkali ferrates has been cited for a century [2-10]. Currently, there is a need for research and innovation in order to improve the existing preparation methods and to develop new methods which would aim to increase the stability and the yield of the latter.

Scholder and al, 1956-b [11] recommended two methods of synthesizing M_2FeO_4 if M is a divalent element (Ba^{2+}, Sr^{2+}) from Fe (III) or from the corresponding alkaline earth metaferrate.

In recent years, a growing number of investigations into the preparation, physico-chemical characterization and detailed performance of certain ferrates (VI). Such as $SrFeO_4$, $BaFeO_4$, Na_2FeO_4, Rb_2FeO_4 and Cs_2FeO_4, have appeared in the literature [12-15]. The solubility of $BaFeO_4$, a salt more commonly studied in connection with super oxidant iron [16].

Recently, S. Licht and al [17] arrived at Ag_2FeO_4, with an unusual intrinsic capacity of 5 electrons was also presented, however, the impurity and instability detract from it as a promising super-iron battery cathode. Attempts to search for alternative ferrate (VI) salts with high intrinsic storage capacity, such as $CaFeO_4$ and $MgFeO_4$, etc. will be encouraging.

Calcium ferrate (VI) powders were synthesized from potassium ferrate (VI) and characterized by titration analysis, elemental analyzer, SEM, XRD, IR, TG and DSC. The results showed that the synthesized sample consists mainly of calcium ferrate (VI) and that calcium ferrate (VI) can exist as $CaFeO_4$ [18]. Also, the maximum purity of $CaFeO_4$ was determined by the modified chromite method [19, 20] was 61.1%.

The total Fe content was determined by the Zimmermann - Reinhardt method [21], using oxidation/reduction titrations with determination of potassium permanganate, and the detailed analytical procedure described in reference [22]. The amount of

Ca^{2+} was determined by an EDTA titration method [23], and K^{+} was determined by the potassium tetraphylboron weight method [24].

According to S. Licht *et al.* [25], calcium ferrate (VI) can exist in the form of $CaFeO_4$, and its corresponding maximum purity obtained is 74.9%. It should be noted that the gradual increase in weight loss between 100 and 400 ° C may be mainly due to the occurrence of a reaction.

$$\mathbf{2\ CaFeO_4 .xH_2O \rightarrow Fe_2O_3 + 1.5O_2 + 2Ca(OH)_2 + (2x\text{-}2)H_2O}$$

$$\mathbf{Ca(OH)_2 \rightarrow CaO + H_2O}$$

The poor stability of the calcium (VI) ferrate sample may be due to its relatively higher Fe (III) impurity [17], crystalloid and / or absorbent water, and the stronger polarization effect of Ca^{2+} ion on FeO_4^{2-} [26].

MATERIAL AND METHOD

The synthesis of $CaFeO_4$ is carried out by dissolving the sodium ferrate salt prepared Na_2FeO_4 in an aqueous solution of calcium nitrate at pH below 12, temperature from 0° C to 40 ° C for 30 minutes in order to obtain a white precipitate which Calcium salt deposits spontaneously and immediately at the bottom of the tube, according to the ion exchange reaction of ferrate VI salt with calcium nitrate:

$$\mathbf{M_2FeO_4 + Ca\ (NO_3)_2 \rightarrow CaFeO_4 + M_2(NO_3)_2}$$

The white precipitate was filtered through filter paper, and washed three times with deionized water. The resulting product, $CaFeO_4$, was dried for 5 h under vacuum at room temperature to give the exact mass of $CaFeO_4$.

As well as the analysis of the purity of the product $CaFeO_4$ was determined by chromite analysis and UV spectrometer.

Chromite analysis determines that the material is 98.7% pure based on the redox state and the remaining iron is in a lower valence state, although at these relatively low concentration levels, nature specific to this ferric impurity is difficult to distinguish. It can be assumed that the excess iron exists as several amorphous ferric salts which can be generalized as a 1.3% ferric oxide impurity.

The preparation of Na_2FeO_4 is done by mixing hydrated iron sulfate $FeSO_4$, $7H_2O$ and concentrated ClO^- bleach at 48°F in the presence of NaOH. The mixture is stirred for one hour at a temperature of around 55 ° C depending on the reaction:

$$\mathbf{FeSO_4, 7H_2O + 4OH^- + 2\ Cl^- \rightarrow FeO_4^{2-} + 9\ H_2O + SO_4^{2-} + 2\ Cl^-}$$

The Na_2FeO_4 is recovered by vacuum filtration. This phase is dried at 120 ° C for 12 hours and then placed in a desiccator for at least one hour before grinding [27], the dried Na_2FeO_4 product has been found to be stable in time, and can be used for calcium ferrate syntheses directly or after storage, since calcium ferrate compounds can be chemically synthesized by conversion from sodium ferrate salts, via a substitution reaction with calcium nitrate. The best results were obtained when sodium ferrate, Na_2FeO_4, was used for the synthesis of $CaFeO_4$.

The phase found was analyzed and followed over time with UV spectrophotometry by measuring the optical density at 507 nm, which is used according to tsapin et al [28], to measure the optical density of the ferrate solution (VI) is done at a wavelength of 507 nm at a pH greater than 10. The characteristic peak of iron (VI) comes out at this wavelength, as well as the volumetric titration method which is based on the oxidation of a chromite salt with ferrate VI according to the reaction below.

$$\mathbf{Cr(OH)_4^- + FeO_4^{2-} + 3H_2O \rightarrow Fe(OH)_3.\ (H_2O)_3 + CrO_4^{2-} + HO^-}$$

The resulting chromate is titrated with a ferrous salt solution with sodium diphenylamine sulfonate as an indicator [29].

The percentage of the original iron-containing material, which is converted to the solid Fe (VI) salt, was determined by the chromite method [30], to probe both the valence state of silver and iron, measured by the reaction of salt to oxidize chromite. The generated chromate is then titrated with a standard ferrous ammonium sulfate solution, using a sodium diphenylamine sulfonate indicator.

RESULTS

The yield of the reaction of the synthesis of the $CaFeO_4$ phase as a function of the pH and the temperature of the reaction medium gives an idea of the progress of the synthesis reaction (figure 1.2).

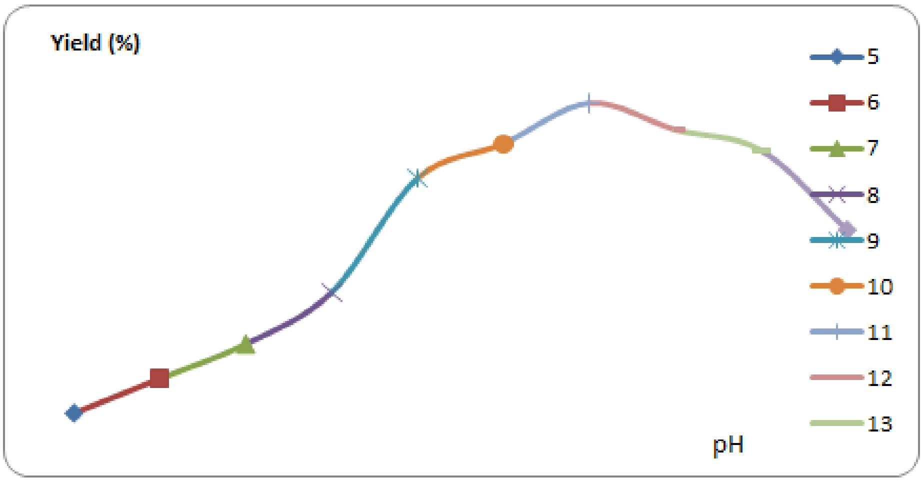

Fig-1: Yield of the reaction of the synthesis of ferrate (VI) $CaFeO_4$ as a function of the pH of the reaction medium

According to the curve (Fig. 1), it can be seen that the yield of the ferrate (VI) obtained increases as a function of the pH of the reaction medium up to 98.71% at the value of pH = 11, which implies that the optimum pH of the synthesis reaction medium is around pH = 11.

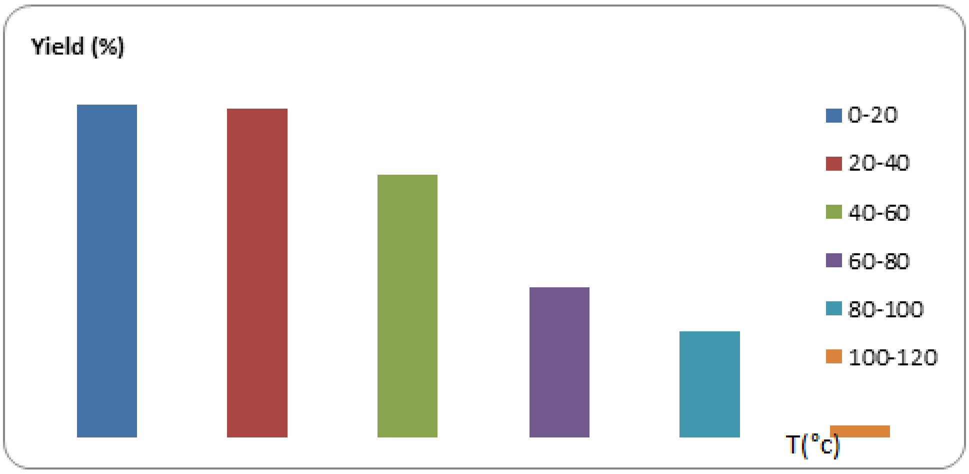

Fig-2: Yield of the reaction of the synthesis of ferrate (VI) $CaFeO_4$ as a function of the temperature of the reaction medium

From the curve (Fig. 2), it can be seen that the yield of ferrate (VI) decreases with the increase in temperature from [40 °C - 60 °C], which implies that the optimum temperature of the The middle of the synthesis reaction is around [0 °C - 40 °C], because in this temperature range the yield reaches its maximum.

Monitoring of the degradation of ferrate as a function of time

The $CaFeO_4$ degradation monitoring results show that the storage time can reach 12 months with a degradation rate in the first six months is limited to 2%.

The results of calculating the rate of degradation between the months and between the state of production and ferrate (VI) and the different months of storage are given in Table 1.

The relation which makes it possible to calculate the percentage of degradation of Iron (VI) is given by the following formula:

$$\%\ \textbf{iron (VI) degradation} = (D.O_i - D.O_f)/D.O_i$$

$D.O_i$: Optical densities of iron (VI) respectively in the initial state
$D.O_f$: Optical densities of iron (VI) in the final state

Tables-1: Optical density of the solution of ferrates (VI) of the synthesized phase $CaFeO_4$ according to the rate of degradation between the initial state of production and different months of storage of ferrate VI (%) as well as according to the rate degradation between months of storage of ferrate VI (%).

t (Months)	The rate of deterioration from baseline in the production and storage of different month ferrate VI (%)	The monthly rate of degradation ferrate VI (%)
1	**0,5**	**0.5**
2	**0.7**	**0.2**
3	**1**	**0.3**
4	**1.2**	**0.2**
5	**1.5**	**0.3**
6	**2**	**0.5**
7	**2.3**	**0.3**
8	**2.8**	**0.5**
9	**3**	**0.2**
10	**3.4**	**0.4**
11	**3.5**	**0.1**
12	**3.9**	**0.4**

According to these results (tab. 1), we notice that the rate of degradation of iron (VI) remains variable as a function of time and varies in a different way from one month to another during storage, which means that the change climatic influences the rate of degradation of ferrate (VI) due to changes in humidity as well as crystalloid and / or absorbent water, and the stronger polarization effect of the Ca^{2+} ion on FeO_4^{2-}.

DISCUSSION

The pH necessary for the synthesis of iron (VI) stable at room temperature for a yield of 98.7% is of the order of 11 (Figure 1), this is compatible with the results of the various preliminary studies [17, 18, 31], which show that the adjustment of the pH, the modification of the concentrations of the reagents and the improvement of the filtration and washing procedures for the synthesis of $CaFeO_4$ by the wet route is required, as well as the purification is important on the stability of $CaFeO_4$.

The optimum temperature, which is around [0°C- 40°C], for the synthesis of $CaFeO_4$ (Fig. 2) is an encouraging progress for the development of industrial processes for the production of ferrates (VI). This result confirms the studies made by Zhihua Xu and col, 2007 [18, 31]. As well as the decrease in impurities results in better stability and increases the discharge performance of the calcium ferrate (VI) sample with a greater intrinsic capacity and a better flow capacity.

Climate change also influences the rate of degradation and the storage time of ferrate (VI) at room temperature, this is compatible with crystalloid and / or absorbent water, and the stronger polarization effect of the Ca^{2+} ion on FeO_4^{2-} [22].

CONCLUSION

This manuscript reviews the most suitable method for the synthesis of ferrate (VI) $CaFeO_4$stable at room temperature from the reaction of calcium nitrate $Ca(NO_3)_2$ and Na_2FeO_4 whose pH is around 11, at a temperature around [0 °C- 40 °C], and a reaction time of the order of 30 minutes.

The process for the wet synthesis of ferrate (VI) of $CaFeO_4$ from Na_2FeO_4 is a very easy and very promising method, although there is still a need for further technical, economical improvement regarding industrial application.

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