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Rapid Chemical Synthesis of Four Ferrate(VI) Compounds

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The preparation of four novel Fe(VI) salts, including $PbFeO_4$, $ZnFeO_4$, $CdFeO_4$ and $HgFeO_4$ is demonstrated. These Fe(VI) salts were synthesized from a solid phase reaction merely by grinding K_2FeO_4 with M $(C_2H_3O_2)_2.nH_2O$ (M = Pb^{2+}, Zn^{2+}) or M $(NO_3)_2.nH_2O$ (M = Cd^{2+}, Hg^{2+}) at room temperature. A rapid and efficient reaction occurred upon grinding the solid reactants to afford high yield ferrate(VI) salts which were characterized by XRD, EDS and FTIR techniques. All of the synthesized ferrates were rather stable and could be stored at room temperature for more than a month with no significant decomposition.

Keywords: Ferrate, Solid phase, $PbFeO_4$, $ZnFeO_4$, $CdFeO_4$, $HgFeO_4$

INTRODUCTION

Potassium ferrate and other group I and II metal ferrates(VI) have been known for a long time. They are the most stable and well-defined terminal oxo species of Fe(VI). The chemistry of ferrates remains relatively unexplored and only recently a detailed account of their preparation and properties have appeared [1,2]. Potassium ferrate is not stable in aqueous solution. However, it has been shown very lately that the stability can be enhanced greatly when ferrate(VI) was encapsulated in ethyl cellulose and paraffin microcapsules. The encapsulated ferrate(VI) has been used to remove some pollutants from water [3].

The ferrate, FeO_4^{2-}, ion is thermodynamically a stronger oxidant than the common oxidants MnO_4^- and CrO_4^{2-}. Thus, it has been used in various fields such as oxidation of organic substrates [4,5], water disinfection and degradation of organic synthetic pollutants [6]. Super-iron batteries incorporating Fe(VI) cathodes salts with a higher capacity and energy advantage compared to the conventional alkaline batteries have also been recently introduced [7,8].

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To our knowledge, the only ferrate(VI) salts that have been prepared up to now are Na_2FeO_4, K_2FeO_4, Rb_2FeO_4, $SrFeO_4$, $BaFeO_4$, $CaFeO_4$ and Ag_2FeO_4 [8-11]. In most cases, these ferrates are commonly prepared directly from the reaction between an aqueous solution of the acetate or chloride of the metals and potassium ferrate. Such a method lacks generality, however, and attempts at preparing group IIB metals, Pb^{2+} or transition metals (Co^{2+}, Fe^{3+}, Ni^{2+}) ferrates from K_2FeO_4 have failed [12,13].

In this work, we report the synthesis of four new metallic ferrates, including $PbFeO_4$, $ZnFeO_4$, $CdFeO_4$ and $HgFeO_4$ with a purity of 94-98% by a rapid and simple solid phase reaction. The prepared samples were characterized by elemental analysis, XRD and FTIR techniques.

EXPERIMENTAL

Materials

All chemicals were of analytical grade obtained from Merck Chemical Company and used without further purification. Potassium ferrate was synthesized using the method described by C. Li *et al*. [13], giving a purity of about 99% for the recrystallized product. The purity was determined

at the maximum of the ferrate absorption peak of 550 nm using a molar absorption coefficient of 1175 M^{-1} cm^{-1} [15,16].

Instrumentation

FTIR spectra were measured with a BOMEN 102 FTIR as a conventional mixture in a KBr pellet. The spectra are presented after the baseline correction, using as a blank the same KBr pellet, but in the absence of Fe(VI) salts.

Powder XRD data measurement was performed on a Philips Analytical X-ray diffractometer, operating with Cu Kα radiation (λ = 1.54056 A°), with a flat sample holder mounted on a PW 1830 spectrogonimeter. The EDS measurement was carried out on a LEO 1455 VP energy dispersive spectrometer.

Solid Phase Preparation of $M^{II}FeO_4$ Compounds

In this specific synthesis, one equivalent of solid K_2FeO_4 and one equivalent of each of the reactants $Pb(CH_3COO)_2.H_2O$, $Zn(CH_3COO)_2.2H_2O$, $Cd(NO_3)_2.4H_2O$ or $Hg(NO_3)_2.H_2O$ were mixed. The mix was ground in a mortar with a pestle for 5 min. An instant change in the color of the mix was observed upon grinding due to a chemical reaction between the two mixed solids. The mixture was then washed with distilled water (two times × 10 ml) and diethyl ether (two times × 10 ml). The final product was dried for 3 h under room temperature vacuum in a desiccator. This solid phase reactions produced new $M^{II}FeO_4$ salts with almost quantitative yields. The products were characterized by XRD, EDS and FTIR spectroscopy.

RESULTS AND DISCUSSION

The dried K_2FeO_4 was found to be stable in time and may be used as the starting material for the synthesis of other ferrates(VI). However, K_2FeO_4 decomposes spontaneously in aqueous solution to give Fe(III) species. The standard half-cell reduction potential of ferrate ion was estimated to be +2.20 V and +0.72 V in acidic and basic solution, respectively. Thus, ferrate(VI) is more stable in strongly alkaline conditions than in neutral or acidic media. Therefore, the conventional synthesis of insoluble ferrates, such as $BaFeO_4$ or $SrFeO_4$ utilizes the precipitation of these compounds in a neutral or alkaline solution [17].

$$K_2FeO_4 + M(C_2H_3O_2)_2 \longrightarrow MFeO_4 + 2KC_2H_3O_2$$
(M = Sr or Ba)

Applying this conventional method to prepare other ferrate salts such as $ZnFeO_4$ or $PbFeO_4$ was not successful and led to immediate decomposition of potassium ferrate. We, thus, triggered a reaction between K_2FeO_4 and the appropriate salts, $Pb(CH_3COO)_2.H_2O$, $Zn(CH_3COO)_2.2H_2O$, $Cd(NO_3)_2.4H_2O$ or $Hg(NO_3)_2.H_2O$ in the solid phase instead of starting the double replacement reaction in aqueous media. Interestingly, an immediate and efficient reaction occured merely upon grinding the solid reactants at room temperature. The replacement reactions which took place are shown below.

$$K_2FeO_4 + M(C_2H_3O_2)_2.nH_2O \longrightarrow MFeO_4 + 2KC_2H_3O_2 + nH_2O$$
$M = Pb^{2+}$ or Zn^{2+}

$$K_2FeO_4 + M(NO_3)_2.nH_2O \longrightarrow MFeO_4 + 2KNO_3 + nH_2O$$
$M = Cd^{2+}$ or Hg^{2+}

Apparently, the presence of bound water included within the used hydrated salts of the metals facilitates the reaction of the ground mixture yielding almost pure $M^{II}FeO_4$ products. The presence of a trace amount of water was crucial for the solid phase reaction to proceed. This was demonstrated by the fact that no reaction was observed on the grinding of anhydrous mercury(II) or cadmium(II) acetates with potassium ferrate. Using solid state reactants has several advantages, such as, fewer preparatory steps which would increase the yield of Fe (VI) salts. Moreover, solutions of K_2FeO_4 are susceptible to degradation to Fe(III) due to a trace of Ni(II) or Co(II) catalysis [18]. This can be virtually avoided by utilizing solid reactants to minimize any solution contact time.

The FT-IR spectra, measured in KBr pellets of the as-prepared $ZnFeO_4$, $CdFeO_4$, $HgFeO_4$ and $PbFeO_4$ are shown in Fig. 1. The IR absorption of the Fe(VI) compounds, K_2FeO_4, are attributed to stretching frequencies of four equivalent symmetrically distributed oxygen atoms surrounding the iron in a tetrahedral manner [19]. As shown in Fig. 1**,** the FTIR spectra are readily distinguishable and all of the four newly synthesized Fe(VI) salts show the characteristic absorption

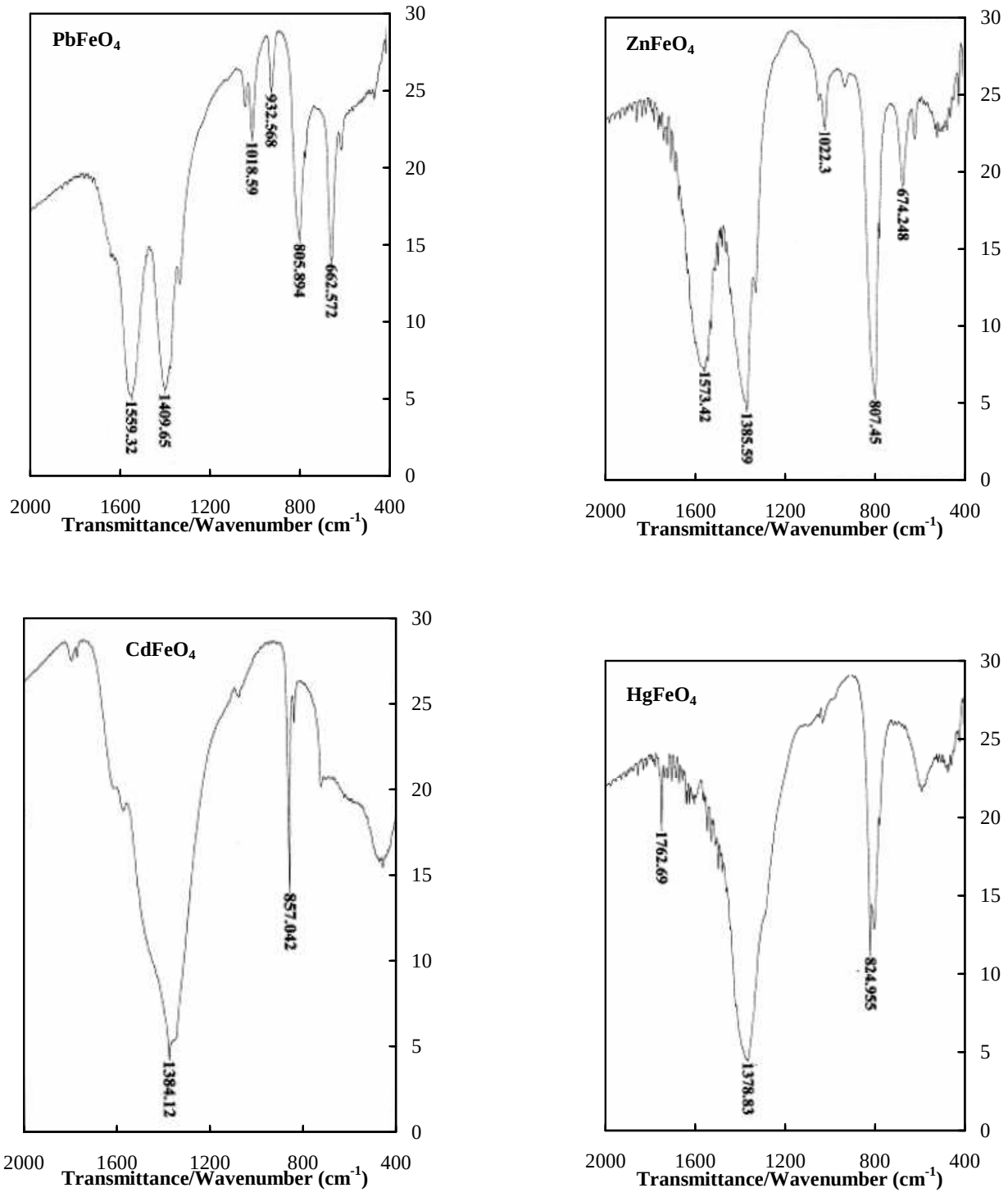

Fig. 1. FTIR spectra of as-prepared Fe(VI) salts.

peaks in the 800 to 850 cm^{-1} range. This observation is consistent with the previously reported FTIR measurements [20]. All these ferrates also exhibit a broad peak at around 1400 cm^{-1}. No clear explanation can be given regarding this peak in the IR spectra and further study is required to carry out a definitive analysis of the absorptions. As a matter of fact, silver ferrate, which has been recently reported, and is the only known ferrate of a transition metal, also displays a similar IR absorption peak in 1400 cm^{-1} region. There is no comment about this peak in the report [9].

Quantitative elemental analysis of the as-prepared ferrate samples was also carried out with an energy dispersive spectrometer. The EDS patterns of the four new metallic ferrates are shown in Fig. 2. As it can be clearly seen, the EDS patterns demonstrate that the four analyzed samples contain only oxygen, iron and one of the metals, Zn, Cd, Hg or Pb. All the residual salts produced by the replacement reaction were thoroughly removed by washing with deionized water.

Figure 3 shows the XRD patterns of the as-prepared ferrate(VI) metallic salts. Although these compounds were prepared by grinding K_2FeO_4 with the corresponding metal salt powders, each of the samples is significantly crystalline as evident from the sharpness of their XRD spectra. The XRD spectra of these ferrate(VI) compounds are different from the reported XRD spectrum of K_2FeO_4 [17].

CONCLUSIONS

In this study, four new ferrate(VI) salts were successfully prepared by a rapid and efficient method utilizing solid sate reactants. In this solid phase conditions, no significant decomposition of the K_2FeO_4 precursor was observed. Thus, this method is much superior to the conventional solution reactions in which the decomposition of K_2FeO_4 is almost unavoidable. Moreover, the as-prepared Fe(VI) salts were rigorously stable and could be stored for more than one month at room temperature with no significant decomposition. It is worthwhile, therefore, to utilize these newly synthesized ferrates as cathodes in super-iron batteries to examine their discharge capabilities.

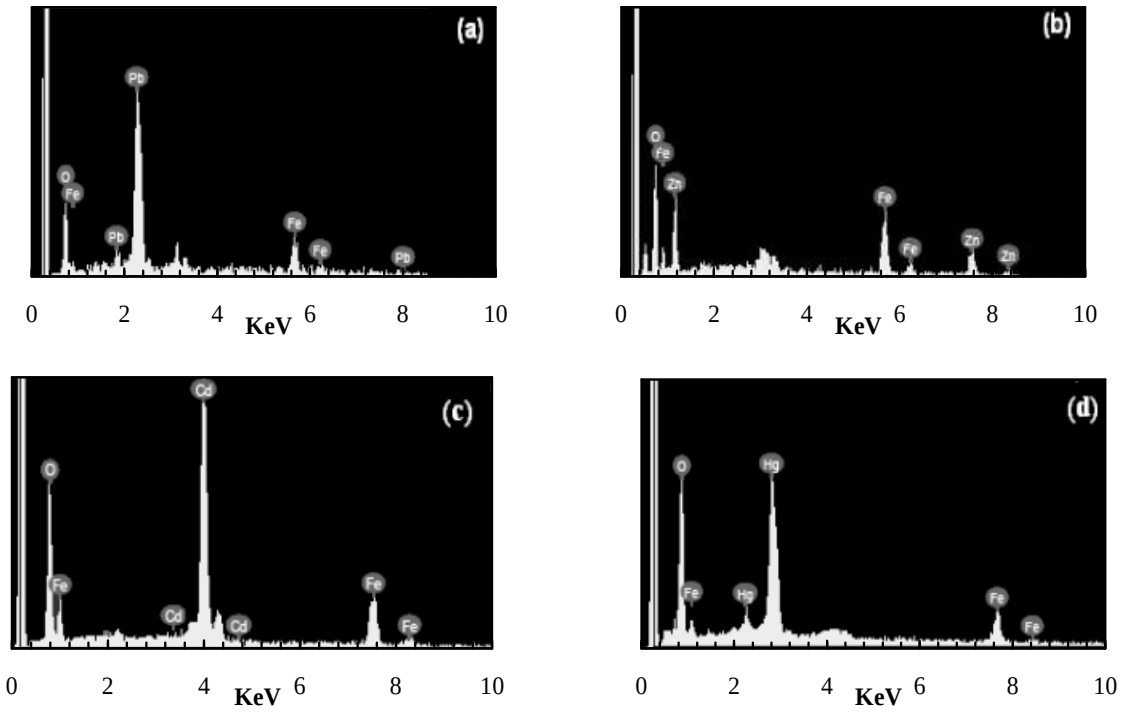

Fig. 2. EDS patterns of the as-prepared ferrate compounds, (a) $PbFeO_4$, (b) $ZnFeO_4$, (c) $CdFeO_4$ and (d) $HgFeO_4$.

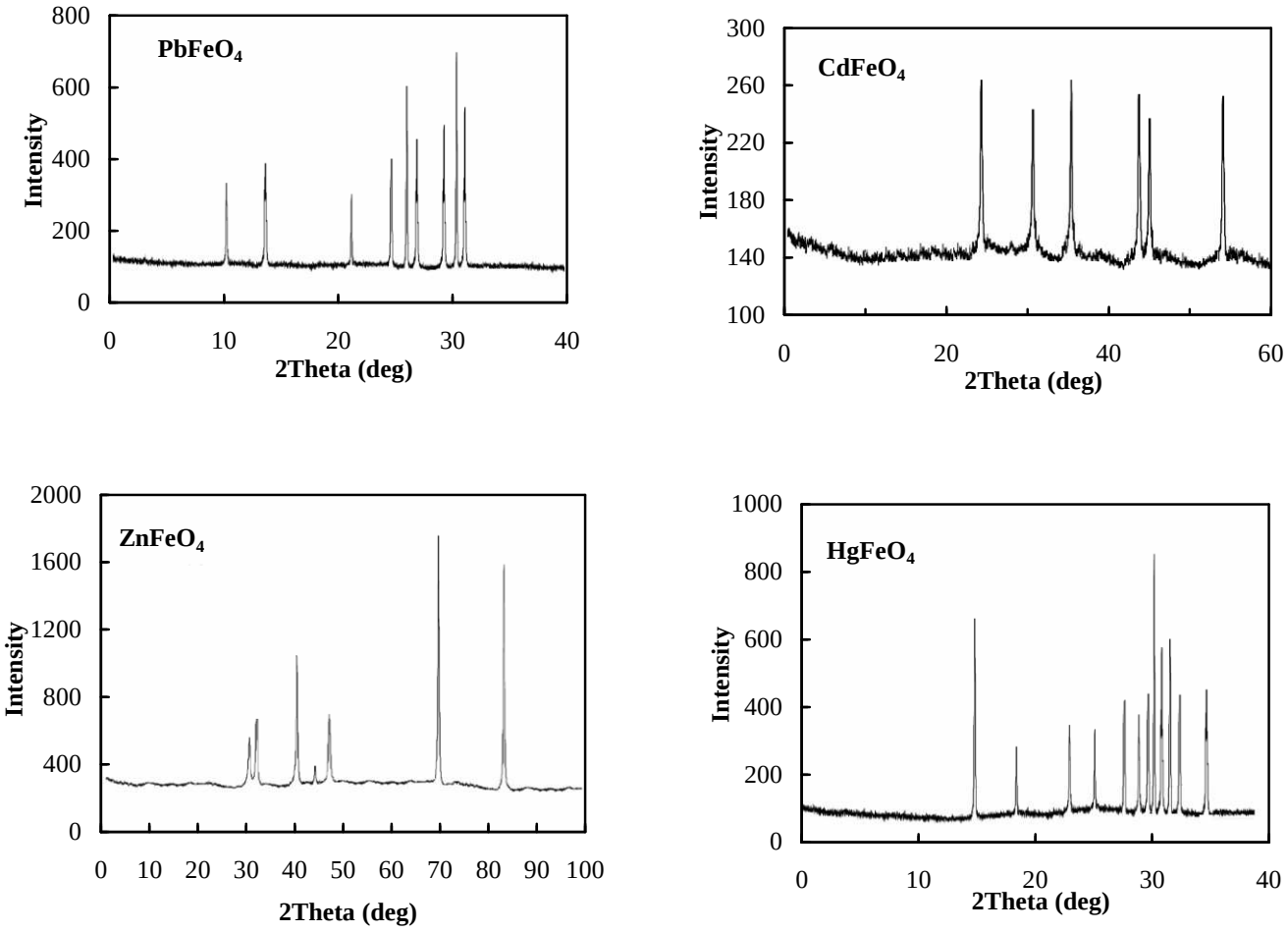

Fig. 3. X-ray powder diffraction spectra of as-prepared samples.

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