Synthesis of Potassium Ferrate by Chemical Dry Oxidation and Its Properties in Degradation of Methyl Orange

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Potassium ferrate(VI) (K_2FeO_4) was successfully synthesized *via* improved chemical dry oxidation method using sodium peroxide (Na_2O_2) and ferric oxide (Fe_2O_3) and the product was characterized by ICP, XPS, XRD, FTIR, UV/VIS and SEM. The experimental results indicated that the synthesized potassium ferrate(VI) had an orthorhombic crystal structure space group, D_{2h} . The yield of the synthesized K_2FeO_4 was 26.7 % (calculated according to Fe) and the purity of the potassium ferrate(VI) reached to 98.7 %. The degradation tests of methyl orange (25 mg/L, 40 mL) were also performed in this work. The results showed that azo organic pollutants, such as methyl orange, could be effectively degraded by K_2FeO_4 .

Key Words: Potassium ferrate(VI), Dry oxidation, Methyl orange, Degraded.

INTRODUCTION

Potassium ferrate(VI) (K_2FeO_4) is an advanced oxide. With strong oxidizability, good flocculability, outstanding adsorbability and effective disinfection property, it has great potential to be used as an environmentally friendly water-treatment agent¹⁻⁷.

Commonly, three methods are usually adopt to prepare ferrate(VI): (a) chemical wet oxidation method⁸⁻¹⁰, by oxidizing a ferric compounds under strong alkaline condition and using hypochlorite as the oxidant; (b) electro-chemical method¹¹, by anodic oxidation using iron or alloy as anode and KOH as electrolyte; (c) chemical dry oxidation method¹²⁻¹⁵, by calcining various iron containing compounds with strong oxidant. Among these methods, the chemical wet oxidation and the electrochemical oxidation methods have many disadvantages, such as large amounts of chemical wastes, limit of the electrode materials and serious environmental pollution *etc.*

However, the chemical dry oxidation method is considered as a fast, environmentally friendly method to prepare ferrate(VI). Compared with the other two methods, the chemical dry oxidation method has many advantages *viz.*, simple reaction equipment, handy operation process, less consumption of raw materials, fewer side reactions and completely environmentally friendly. Yet limited reports about this method are available in literature. Tamayo *et al.*¹³ found that Na_2FeO_4 could be prepared by calcining the mixture of

$FeSO_4$ and Na_2O_2 at 700 °C for 1 h. The reaction of the method is as follow:

In addition, Kiselev *et al.*¹⁴ suggested that K_2FeO_4 could be obtained by calcining the mixture of Fe_2O_3 and K_2O_2 at 350-370 °C. The reaction equation is as follows:

In this study, the above-mentioned chemical dry oxidation method to prepare ferrate(VI) was evolved in several aspects: Firstly, we adopt temperature-programmed method to prevent excessive heating of the reaction system; Secondly, Na_2O_2 and Fe_2O_3 were used to replace K_2O_2 and $FeSO_4$, because Na_2O_2 is more stable and less corrosion to the reactor than K_2O_2 . Besides, Fe_2O_3 is more easily oxidized than $FeSO_4$ and no SO_3 is going to be produced; Thirdly, the calcined solid product were dissolved in aqueous KOH instead of NaOH to simplify the purification process. With these aspects, the quality of the product could be significantly improved. In addition, this study also reported on the results of laboratory experiments involving the degradation of methyl orange (MO), a typical azo dyes structure, by the synthesized K_2FeO_4 .

EXPERIMENTAL

The main chemicals used were ferric oxide (Fe_2O_3), sodium peroxide (Na_2O_2), potassium hydroxide (KOH) and

methyl orange. All chemicals used in this study were analytical reagent grade without further purification. The used solutions were prepared with distilled water.

Preparation of potassium ferrate(VI): Sufficient Na_2O_2 and Fe_2O_3 were mixed together in a molar ratio of 6:1 ($\text{Na}_2\text{O}_2/\text{Fe}_2\text{O}_3$). Then the mixture was calcined in a stainless steel tubular furnace in the flow of dry oxygen (carbon dioxide free). The calcining temperature was increased from 28 to 700 °C with a step of 6 °C/min and maintained at 700 °C for 1 h. Considering the hygroscopic property of sodium peroxide and potassium ferrate, all performance was handled rapidly in a dry environment.

Ten grams of the calcined solid product were dissolved in 40 mL of KOH solution (5 M) and kept the temperature of the solution under 5 °C. The formed purple-dark solution was quickly stirred for 2 min for ensuring that the sample was dissolved in the KOH solution completely. Then the obtained solution was filtered through a G3 sand core funnel with large surface area to shorten the time of filtration and the filtrate was filtered again through a G4 sand core funnel. The filtrate was collected in a beaker containing 100 mL of saturated KOH solution. This process must be performed at 20 °C to prevent the crystallization of KOH. After 10 min of stirring and 30 min of settlement, the filtrate in the saturated KOH solution was filtered through a G3 sand core funnel. The purple-black precipitate was rinsed in sequence with 25 mL of *n*-hexane, 10 mL of methanol and 10 mL of diethyl ether. Each solvent washing process was conducted for four times. The final product, solid K_2FeO_4 , was collected and stored in a vacuum desiccator prior to further use.

Degradation of methyl orange: Degradation of methyl orange was carried out by quickly mixing aqueous methyl orange (25 mg/L, 40 mL) and ferrate(VI) in a 150 mL glass beaker. After mechanic stirring for a certain time, sodium sulfite was added to the mixture to stop the reaction. Then the sample was centrifuged at 4500 rpm for 10 min and then filtered for analysis. All the experiments were carried out at room temperature (23 ± 2 °C).

The degradation rate D (%) of methyl orange was calculated as the following formula:

$$D(\%) = \frac{(A_0 - A)}{A_0} \times 100 \text{ } ^\circ\text{C} \quad (3)$$

where A_0 and A are the intensity of the maximum absorption wavelength of the aqueous methyl orange before and after degradation, respectively.

Analytical methods: The solid ferrate(VI) was quantitatively analyzed by the chromate titration method¹⁶. Purity P (%) and yield Y (%) of the ferrate(VI) in the sample were calculated as follow:

$$P = \frac{(\text{CFe}^{2+} \times \text{NFe}^{2+}) \times M_{\text{sample}}}{3000m_{\text{sample}}} \times 100\% \quad (4)$$

$$Y = \frac{m_a}{m_t} \times 100\% \quad (5)$$

where M_{sample} is the molar mass of K_2FeO_4 (198.04 g mol⁻¹). m_{sample} represents the weight of the sample, while m_a and m_t

are the actual weight and theoretical weight of K_2FeO_4 , respectively.

Inductively coupled plasma analysis of the sample was conducted with an ICP Pekin-Elmer Optima 3000DV and 100 mg of sample was used. X-ray photoelectron spectroscopy (XPS) (V.G.ESCA Mark II) of the sample was operated at a pass energy of 50 eV and a step size of 0.05 eV using AlK_{α} radiation. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2500 recording diffractometer with CuK_{α} radiation (40 kV, 30 mA, wavelength $\lambda = 0.15418$ nm), nickel filter, angle range of scanning was from 10° to 80° and at a scanning rate of 8° min⁻¹. FTIR spectrum was measured on a Nicolet-Impact 400 Fourier transform infrared spectrometer in a conventional KBr pellet and a range of 4000-400 cm⁻¹ was scanned. The morphology of the sample was examined by scanning electron microscopy (SEM) with a XL30 microscopy (FEL, Holland). The photoscopy of the sample in aqueous was determined by UV-1700 spectrometry, data were recorded over a range of 300 to 800 nm. The maximum absorbance of the aqueous methyl orange was determined by UV-1700 spectrometer.

RESULTS AND DISCUSSION

ICP analysis: The calculation results of the final product is given as below: the purity (P) of K_2FeO_4 is 98.7 %, the yield (Y) is 26.7 % (calculated according to Fe) and some ICP results are summarized in Table-1. As can be seen in Table-1, K and Fe are the principal elements in the final product. The respectively mass percentages are 39.5 % for K and 28.1 % for Fe. Sodium is the main impurity, which has a mass percentage of 0.13 %. According to the calculation, we find that the molar ratio of K/Fe is 2.018, which implies that the formula of the product is K_2FeO_4 .

TABLE-1
ICP DETERMINED ELEMENTAL CONSTITUENTS
MEASURED IN THE FINAL PRODUCT

Sample	Mass (mg)	K by mass (%)	Fe by mass (%)	Na by mass (%)
Final product	100	39.5	28.1	0.13

XPS analysis: Fig. 1 displays the XPS spectra of the iron ions and oxygen ions on the surface of the final product, respectively. It can be seen from Fig. 1(a) that the bonding energies of $\text{Fe}_{2p_{3/2}}$ and $\text{Fe}_{2p_{1/2}}$ appear at 712.8 eV and 725.5 eV. The $\text{Fe}_{2p_{3/2}}$ peak is shifted by *ca.* 1.8 eV, 0.6 eV and 0.4 eV to higher binding energies than those of Fe(III), Fe(IV) and Fe(V)¹⁷. This phenomenon indicates that more strong interaction between electrons and nucleus is due to the increased in Fe valence state. Thus the XPS spectrum of the sample shows that on the surface, the iron ions are VI valence too. As shown in the Fig. 1(b), due to feedback of a part of the oxygen atom valence electrons to the iron orbital, the electron density of oxygen atom is reduced. Therefore, its binding energy is increased (the binding energy of the O1S in iron oxide is 530 eV). Meanwhile, there is a shoulder peak at 531.0 eV, which can be attributed to O1S caused by a few H_2O absorbed on the surface.

Fig. 1. XPS spectra of the final product [(a) Fe_{2p}, (b) O_{1s}]

X-ray diffraction analysis: X-ray powder diffraction spectrum of the final product is presented in Fig. 2. The peaks at 29.97°, 30.35°, 28.95° and 20.78° can be indexed to (013), (020), (211) and (111) planes of K₂FeO₄ (JCPDF 25-0652). The result reveals the presence of the K₂FeO₄ as a single phase without any other crystalline compounds. The XRD pattern also indicates that the K₂FeO₄ has an orthorhombic crystal structure with a space group of D_{2h} (Pnma): *a* = 0.7722 nm, *b* = 0.5885 nm and *c* = 1.0363 nm, which was close to the reported values^{18,19}, calculated from eqn. 6.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (6)$$

From the above XRD pattern, it can be seen that the final product prepared by the chemical dry oxidation method is K₂FeO₄.

FT-IR (spectroscopy) analysis: Fig. 3 shows the FT-IR spectrum of the K₂FeO₄. It can be seen that the FT-IR absorption spectrum of the K₂FeO₄ possesses a primary peak at about 808 cm⁻¹ and a shoulder peak at *ca.* 780 cm⁻¹, which attribute to the asymmetric stretching vibrations of the Fe-O bond in the ferrate(VI)²⁰⁻²⁵. In Fig. 3 the intensity of the characteristic vibrational peak of ferrate(VI) is strong, indicating that the purity of the prepared ferrate(VI) is higher. In addition, other

Fig. 2. Typical X-ray diffraction spectra of the K₂FeO₄ Fig. 3. FT-IR spectrum of the K₂FeO₄

vibration peaks in the FT-IR spectrum (Fig. 3) are described as follows. The peaks at 3450 and 1623 cm⁻¹ should be attributed to the characteristic absorption peaks of the H-O bond stretching vibration and bending vibration of water, respectively. The peaks at about 1420 and 890 cm⁻¹ should be assigned to the characteristic absorption peaks of the C-O bond stretching vibration, which was caused by the carbon dioxide in air¹³. While the peak at about 1110 cm⁻¹ may be due to the stretching vibration of the intramolecular bond of ether in diethyl ether, which is the residue derived from the filtration process.

UV/VIS spectra analysis: The UV/VIS absorption spectrum of the dissolved K₂FeO₄ is shown in Fig. 4. Fig. 4 shows that the UV/VIS spectrum is the distinctive UV/VIS spectrum of FeO₄²⁻: two maxima of absorbance at 510 and 785 nm²⁶, an absorption shoulder at 570 nm and two minima of absorbance at 400 and 678 nm. From the UV/VIS spectrum, following conclusions can be drawn: the K₂FeO₄ is instantaneously hydrolyzed to form tetrahedral ions FeO₄²⁻ when it is dissolved in water.

SEM analysis: The SEM micrographs of the K₂FeO₄ are shown in Fig. 5. As can be seen in Fig. 5, the K₂FeO₄ crystals are plump, columnar and have obvious cone-shape growth

Fig. 4. UV/VIS spectrum of the K_2FeO_4 Fig. 5. SEM micrograph of the K_2FeO_4

surface at the two ends of the crystalline grains. This is as same as the β - K_2SO_4 -type orthorhombic unit cell. There is a V-type growth of surface in the c-axis of the crystal, making the growth of this direction more developed. While the growth of β -axis is suppressed, thus it is very thick.

Degradation of methyl orange (MO): The effect of reaction variables such as reaction time, pH of the solution and the K_2FeO_4 amount was studied and results are presented below.

Effect of pH: Experiments were performed to study the influence of pH on the degradation of methyl orange in aqueous. A set of experiments was carried out with 40 mL of aqueous methyl orange (25 mg/L) and 2 mg of K_2FeO_4 at

various pH values from 2 to 12. In each experiment, 60 min of reaction time was proceeded. The experimental results are shown in Fig. 6. It is evident from Fig. 6 that the decomposition of aqueous methyl orange was accelerated with increasing pH value up to 6 (maximum degradation rate, 58.11 %), beyond which the decomposition started to decrease, indicating an optimum pH of *ca.* 6 for best performance.

Fig. 6. Effect of pH on methyl orange (MO) degradation ($C_{MO} = 25$ mg/L; K_2FeO_4 quality = 2 mg; reaction time = 60 min)

Effect of reaction time: The influence of reaction time on the degradation of methyl orange from its aqueous solution was investigated with 40 mL of aqueous methyl orange (25 mg/L) and 2 mg of K_2FeO_4 at pH 6. In each experiment, 60 min of reaction was proceeded. The experimental results are shown in Fig. 7. It can be found from Fig. 7 that the reaction between aqueous methyl orange and K_2FeO_4 was very rapid. The major decomposition of aqueous methyl orange occurred during the first 10 min, the degradation rate reaches to 44.51 %. When the reaction time is increased up to 60 min, the degradation date reaches to 58.11 %. Then it keeps unchanged after 60 min.

Fig. 7. Effect of reaction time on methyl orange (MO) degradation ($C_{MO} = 25$ mg/L; K_2FeO_4 quality = 2 mg; pH = 6)

Effect of the K_2FeO_4 amount: Experiments were performed to study the influence of the K_2FeO_4 amount on the degradation of methyl orange in aqueous medium. A set of

tests was carried out with different amounts of K_2FeO_4 from 1 mg to 10 mg. The pH value of the reaction system was 6 and the reaction time was 60 min. The results are shown in Fig. 8. It can be observed from Fig. 8 that the decomposition of aqueous methyl orange increases sharply with the increase of K_2FeO_4 . When the amount of K_2FeO_4 increases up to 9 mg, the degradation rate reaches to 99.2 %. Then it keeps unchanged when more than 9 mg of K_2FeO_4 is used.

Fig. 8. Effect of K_2FeO_4 quality on methyl orange (MO) degradation ($C_{MO} = 25$ mg/L; pH = 6; reaction time = 60 min)

Based on the above tests, it is clear that aqueous methyl orange can be successfully degraded by K_2FeO_4 and the degradation rate can reach to 99.2 %.

Conclusion

In this study, solid K_2FeO_4 was successfully prepared by an improved chemical dry oxidation method. Various techniques were employed to characterize the sample. The composition of the product is K_2FeO_4 , which has a orthorhombic unit cell structure with the same space group Pnma as β - K_2SO_4 and its cell parameters were calculated as $a = 0.7722$ nm, $b = 1.0363$ nm and $c = 0.5885$ nm. The purity of the synthesized K_2FeO_4 was determined as high as 98.7 % by the chromate titration

method. The yield was *ca.* 26.7 % (calculated according to Fe). Aqueous methyl orange as a simulated azo dye wastewater could be successfully degraded by the synthesized K_2FeO_4 and the degradation rate can reach to 99.2 %, which proved that K_2FeO_4 is an excellent water-treatment agent.

REFERENCES

1. J.D. Rush and B.H.J. Bielski, *J. Am. Chem. Soc.*, **108**, 523 (1986).
2. L. Delaude and P. Laszlo, *J. Org. Chem.*, **61**, 6360 (1996).
3. C. Jeannot, B. Malaman, R. Gerardin and B. Oulladiat, *J. Solid State Chem.*, **165**, 266 (2002).
4. V.K. Sharma, *Adv. Environ. Res.*, **6**, 143 (2002).
5. V.K. Sharma, *Water Sci. Technol.*, **49**, 69 (2004).
6. B. Lei, G.D. Zhou, H.B. Mi, K.J. Zhen and T.X. Cheng, *Asian J. Chem.*, **24**, 209 (2012).
7. V.K. Sharma, S.K. Mishra and N. Nesnas, *Environ. Sci. Technol.*, **40**, 7222 (2006).
8. G.W. Thompson, L.T. Ockerman and J.M. Schreyer, *J. Am. Chem. Soc.*, **73**, 1379 (1951).
9. J.M. Schreyer, G.W. Thompson and L.T. Ockerman, *Inorg. Synth.*, **4**, 164 (1953).
10. D.A. White and G.S. Franklin, *Environ. Technol.*, **19**, 1157 (1998).
11. A. Denvir and D. Pletcher, *J. Appl. Electrochem.*, **26**, 815 (1996).
12. E. Martinez-Tamayo, A. Beltrán-Porter and D. Beltrán-Porter, *Thermochim. Acta*, **91**, 249 (1985).
13. E. Martinez-Tamayo, A. Beltrán-Porter and D. Beltrán-Porter, *Thermochim. Acta*, **97**, 243 (1986).
14. Y.M. Kiselev, N.S. Kopelev, N.A. Zav'yalova and Y.D. Pervil'ev, *Russ. J. Inorg. Chem.*, **34**, 1250 (1989).
15. J. Paul, WO Patent, 06,924 (1992).
16. J.M. Schreyer, G.W. Thompson and L.T. Ockerman, *Anal. Chem.*, **22**, 1426 (1950).
17. W.H. Yang, J.M. Wang, T. Pan, F.H. Cao, J.Q. Zhang and C.N. Cao, *Electrochim. Acta*, **49**, 3455 (2004).
18. R.H. Herber and D. Johnson, *Inorg. Chem.*, **18**, 2786 (1979).
19. C. Li, X.Z. Li and N. Graham, *Chemosphere*, **61**, 537 (2005).
20. P. Tarte and G. Nizet, *Spectrochim. Acta*, **20**, 503 (1964).
21. W.P. Griffith, *Coord. Chem. Rev.*, **5**, 459 (1970).
22. R.J. Audette and J.W. Quail, *Inorg. Chem.*, **11**, 1904 (1972).
23. S. Licht, V. Naschitz, S. Ghosh and L. Lin, *Electrochem. Commun.*, **3**, 340 (2001).
24. W.C. He, J.M. Wang, H.B. Shao, J.M. Zhang and C.N. Cao, *Electrochem. Commun.*, **7**, 607 (2005).
25. Z.H. Xu, J.M. Wang, H.B. Shao, Z. Tang and J.Q. Zhang, *Electrochem. Commun.*, **9**, 371 (2007).
26. J.D. Rush and B.H.J. Bielski, *Inorg. Chem.*, **28**, 3947 (1989).