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Study on the Stability of $FeCl_3$-Graphite Intercalation Compounds Synthesized by Molten Salt Method

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Abstract: The intercalation of $FeCl_3$ into graphite with molten salt method has been synthesized. Its structural stability and thermal stability both in air and some liquid media for some time were investigated by using the XRD as well as TG-DTG techniques. The obtained results show that $FeCl_3$-GICs are quite stable in air, higher stable in water and acid liquid media, but less stable in alkalic liquid media and some organic solvents. The degradation temperature of $FeCl_3$-GICs is about 330 ℃.

Key words: inorganic chemistry; graphite intercalation compound; ferric chloride; stability; molten salt method

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1 Introduction

The field of graphite intercalation compounds (GICs) has been witnessing a tremendous worldwide growth in recent years. The formation of GICs is based on the layered structure of graphite and the difference in layered structure bond strengths. The in-plane C—C distance (0.141 nm) in graphite corresponds to the bond length of aromatic hydrocarbons. On the other hand, the interplanar C—C distance (0.335 nm) is related to the weak Van Der Waals action between the graphite layered structure. Intercalation processes take place by inserting various guest species (including alkali and alkali earth metals, acids, halogens or metal halides) between layers of the graphite host[1]. Due to the chemical and physical properties of GICs, they can used as catalysts, electrode materials in batteries, interference material in electromagnetic counterworks, and/or components electrical power transmission[2]. Up to now, more than 200 GICs have been synthesized in various fields. Because of its highly electrical conductivity, highly magnetic permeability and low specific gravity, $FeCl_3$-GICs are one of the most promising materials used as the broad smoke aerosol to shield or attenuate the infrared/millimeter wave double-mode guidance systems. Here, we pay much attention to its environmental stability and thermal stability for improving engineering application property and safety.

2 Experimental

Natural graphite powder in an average flake size of 5 μm was used as a host. Ferric chloride ($FeCl_3$) powder was heated at 120 ℃ under vacuum for 4 hrs. Graphite and chloride powder were weighed, mixed and sealed in a Pyrex glass tube of calibrated volume. The reaction system was heated at 140 ℃ under reduced pressure for at least 2 hrs to remove all traces of water. Then, the intercalation processes were carried out between 380 ℃ and 500 ℃ for 60 ~ 72 hrs.

The experiments were carried out in molar ratio of $FeCl_3$: C from 1 : 5 to 1 : 20. A large excess of molten salts were kept to ensure the intercalation reaction with graphite[3]. After the reaction was finished, the products were washed with water to remove the excess chlorides clearly, and the obtained products dried at 80 ℃ for 120 hrs.

X-ray powder diffraction was performed on a D/max-RB X-ray powder diffract meter by using K_α radiation of copper (λ_{K_α} = 0.154 178 nm) with Ni-Filtered. The results verified that the obtained GIC generates a very broad

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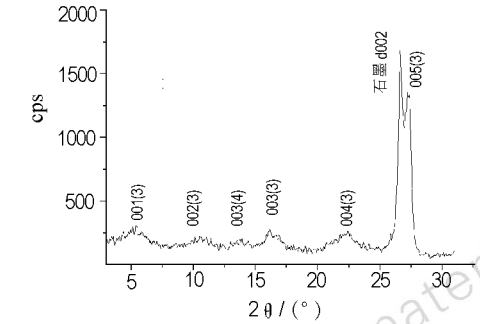
and low-amplitude scattering event between $2\theta = 6°$ and $2\theta = 40°$. The X-ray diffraction patterns were collected in the $\theta/2\theta$ step scanning mode with a step size of 0.02° (2θ). The X-ray powder diffraction patterns were shown in Fig. 1 for products obtained after 60 hrs by reaction of graphite in $FeCl_3$ Melt at 500 ℃. Table 1 and table 2 show that these X-ray diffraction spectra.

Table 1　Theoretical X-ray diffraction spectrum of $FeCl_3$-GIC

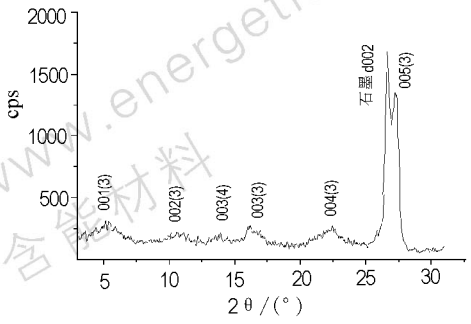
Crystal plane	Stage of GIC		
	2	3	4
(001)	13.02	16.37	19.72
(002)	6.51	8.19	9.86
(003)	4.34	5.46	6.57
(004)	3.26	4.09	4.93
(005)	2.60	3.27	3.75

Table 2　Experimental X-ray diffraction spectrum of $FeCl_3$-GIC

Crystal plane	Stage of GIC		
	2	3	4
(001)	12.81	16.06	19.61
(002)	6.34	8.12	9.83
(003)	4.22	5.43	6.48
(004)	3.20	3.92	4.82
(005)	–	3.28	–



(a) Stage-2 $FeCl_3$-GIC



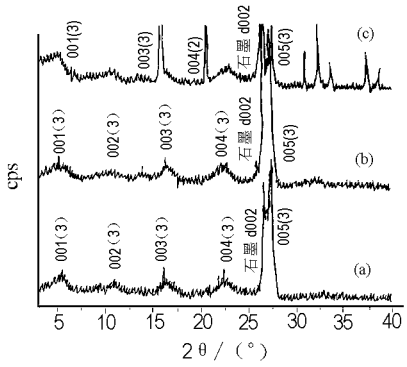
(b) Stage-3 $FeCl_3$-GIC

Fig. 1　X-ray diffraction patterns of $FeCl_3$-GIC

3　Results and discussions

3.1　Stability of $FeCl_3$-graphite in air

The environmental stability of $FeCl_3$-GIC was tested in air for 30 days. The XRD patterns of $FeCl_3$-GIC show little change compared to the as-prepared products. It was proved that higher stage of GIC is, better electrical conductivity is[4]. Therefore, the stage-3 of GIC is the main target. Fig. 2 shows that the diffraction patterns of stage-3 GIC as well as as-prepared intercalation compound. The test results suggest that $FeCl_3$-GIC is very stable exposed to air in 30 days. Otherwise, when the products were exposed in air for 180 days, the XRD patterns of the intercalation compound showed only a little line broadening, shift and stage conversion from the second and third to higher stage.



(a) the sample immerged in water for 6 days
(b) the sample after 6 days in 0.1 mol/L acid
(c) the sample after 7 days in 0.1 mol/L sodium hydroxide

Fig. 2　X-ray diffraction patterns of $FeCl_3$-GIC exposed to the air

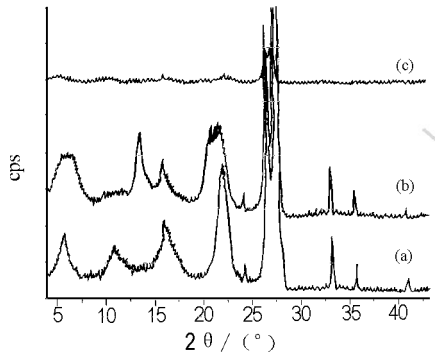
3.2　Stability of $FeCl_3$-graphite in media

Stage-3 of $FeCl_3$-GIC was immerged in water, acidic, alkaline and organic solvent, respectively. After the GIC were tested in water, in 0.1 mol/L hydrochloric acid and in CCl_4, for 6 days, the XRD pattern of the tested GIC are almost same as the pattern of the as-prepared GIC as shown in Fig. 3. When the GIC was contacted with sodium hydroxide solution for 7days, the stage-3 of $FeCl_3$-GIC is highly unstable under ambient conditions and shows significant decomposition. X-ray diffraction measurements show the graphite occurred stage conversions and partial deintercalation. One of the reasons that cause the phe-

nomena of deintercalation is the equilibration reaction of $FeCl_3$ and water:

$$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+ \quad (1)$$

When adding sodium hydroxide, above equilibrium reaction shifts rightward. So the ferric chloride intercalated in the graphite will be withdrawn out and the relevant XRD diffraction spectra appear small changes.



(a) the as-prepared GIC
(b) exposed in air for 30 days
(c) exposed in air for 180 days

Fig. 3 X-ray diffraction patterns of $FeCl_3$-GIC exposed to the media

3.3 Thermal stability of $FeCl_3$-graphite

The obtained stage-3 $FeCl_3$-GIC was tested with TG techniques, and result was shown in Fig. 4.

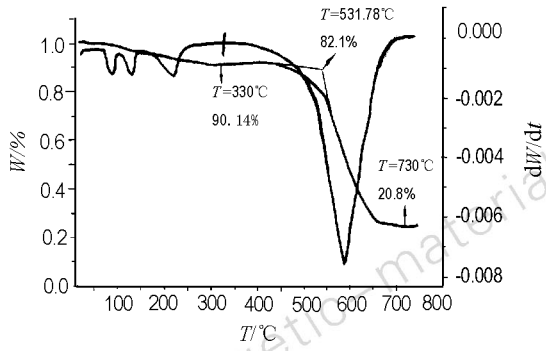


Fig. 4 TG-DTG curves of $FeCl_3$-GIC tested in atmosphere with a heating rate of 15 ℃ · min^{-1}

The TG results indicates that the $FeCl_3$-GIC with a stage 3 structure remained stable until it started to lose mass from 150 ℃ to 190 ℃, the intercalate species started to decompose and GIC was exfoliated between 330 ℃ and 380 ℃. The total mass loss rises from 1.1% to 4.4%. From then on, TG curve started to decline and loss mass sharply. The total mass loss rises from 12.1% to 79.5%. The above-mentioned data show that the decomposition temperature of $FeCl_3$-GIC is about 330 ℃. The mass loss of GIC below 330 ℃ resulted from the losing of absorbed and crystallized water both in graphite and $FeCl_3$. Graphite was slowly oxidized between 400 ℃ and 640 ℃ and led to loss mass.

4 Conclusion

According to experimental results, the major findings are summarized as follows:

(1) $FeCl_3$-GICs with stage 2 to stage-4 structures were synthesized with molten salt method as evidenced by X-ray powder diffraction.

(2) $FeCl_3$-GIC is very stable in the air, acid media and organic solvent, but less stable in alkaline liquor and ferric chloride. The TG-DTG results show that $FeCl_3$-GIC will decompose from 330 ℃.

(3) The stage-3 of $FeCl_3$-GIC has a good environmental stability and thermal stability. It can meet the demand of reliable and security used in interference material, it would be used as the new military aerosol material.

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4 结果与讨论

铜粉应分批加入,铜粉的加入速度应控制在使反应液温度保持在 180 ~ 185 ℃。温度过低不能激活反应;温度过高则会使 PNP 炭化,影响产品性能。反应过程中,要通入氮气保护,以防止铜粉再次被氧化而失活,从而导致聚合物的聚合度降低。后处理过程中,减压蒸馏应在混合物处于粘稠状态时停止,否则会出现炭化现象。乙醚溶胀时间要保证至少 2 ~ 3 h,以确保 PNP 充分溶胀,同时也可以减少水蒸汽蒸馏的时间。最后得到的产品热分解温度为 329 ℃,堆积密度为 0.61 $g \cdot ml^{-1}$。

在 DCTNB 的合成中加热采用水浴代替油浴,温度控制较文献[5]更为灵活一些,得到的 DCTNB 质量有所提高。PNP 的合成温度由文献[4]的 150 ℃提高到 180 ℃,使分子量也得到提高。

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Synthesis of Polynitropolyphenylene

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Abstract: The good properties of non-crystalline state, high thermal stability, and high energy have made polynitropolyphenylene(PNP) a promising energetic polymer in the field of explosives and propellants. PNP was synthesized *via* polymerization using dichlorotrinitrobenzene as starting material. The important parameters affecting the polymerization were analyzed and dicussed in this paper. The obtained relative molecular mass of PNP, thermal decompostion temperature, and bulk density were all determined.

Key words: organic chemistry; synthesis; polynitropolyphenylene(PNP); energetic polymer; dichlorotrinitrobenzene(DCTNB)

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熔盐法合成 $FeCl_3$-石墨层间化合物的稳定性研究

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摘要:采用熔盐法合成出 $FeCl_3$-石墨层间化合物,将其在空气或某些液体媒介中放置一段时间,运用 XRD、TG-DTG 测试技术研究了 $FeCl_3$-GIC 的结构稳定性与热稳定性。结果表明,$FeCl_3$-GICs 在空气中很稳定,在水、酸溶液中具有较好的稳定性,但在碱性溶剂及某些有机溶剂中不稳定。$FeCl_3$-GICs 的热分解温度约为 330 ℃。

关键词:无机化学;石墨层间化合物;三氯化铁;稳定性;熔盐法

中图分类号:TQ567.5 **文献标识码**:A