

Preparation of ferric - doped expandable graphite and study on its catalytic activity

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Abstract: In order to prepare ferric -doped expandable graphite (GIC₁) and to investigate its catalytic activity for the synthesis of isoamyl acetate, GIC₁ was prepared with 50 mesh natural graphite as raw materials, potassium permanganate as the oxidant, vitriol and ferric chloride as intercalation reagent. The influential factors on GIC₁ catalytic activity such as temperature, the amount of KMnO₄, H₂SO₄ (75%) and FeCl₃ were investigated by the orthogonal test. XRD was adopted to characterize different kinds of graphite. Take esterification rate as the priority object, the feasible material proportion in the preparation of GIC₁ is: C: KMnO₄: H₂SO₄ (75%): FeCl₃=1: 0.34: 3.9(75%): 0.15. The intercalation reaction is carried out at room temperature for 60 minutes, and the yield of isoamyl acetate reaches 86.0% with the GIC₁ used as solid acid catalyst. The research indicates that GIC₁ show higher catalytic activity for the esterification of acetic and isoamyl alcohol, and it is recycling and reusable.

Keywords: Expandable graphite, Ferric chloride, Solid acid, Isoamyl acetate, Catalytic activity.

INTRODUCTION

Ferric compounds can be used in a series of esterification reactions as acid catalyst^[1, 2]. It is generally soluble in water and shows better catalytic activity. In order to make it reusable, ferric compounds should be intercalated into suitable carriers such as active carbon or silica gel^[3, 4]. Expandable graphite is a kind of composite material which is formed by inserting heterogeneous molecules, atoms and ions into graphite layers, so it is called graphite intercalation compound (GIC). As a kind of solid -acid catalyst in organic reactions^[6, 7], GIC functions in two ways, one is the GIC acting as pure catalyst; another is the intercalation reagent acting as reactant. The former has two kinds of cases: no change or taking part in intermediate reaction but restoring to the original state

in the end. Different inserting methods or forms of the intercalation compound will lead different catalytic activity of GIC. In the preparation of GIC with FeCl₃ as intercalation reagent of raw graphite^[8], Wang gave the reaction condition of C: 96%H₂SO₄: KMnO₄: FeCl₃=1: 3.0: 0.8: 0.15. The reaction was carried out at 50°C for 60 minutes, and the expansion volume of GIC was 230mL/g. According to Ren-hui^[9], magnetic ferric -doped expanded graphite was prepared by dipping, stirring and standing expandable graphite in ferrocene then expanding at 500°C, and it can be used to prepare magnetic material with better interference property for millimeter microwave. In the paper, ferric-doped expandable graphite GIC₁ was prepared with 50 mesh natural graphite as raw material, KMnO₄ as

oxidant, H₂SO₄ and FeCl₃ as intercalation reagent. In this way, the preparation of GIC and the intercalation of ferric compound were combined, and its' catalytic activity for esterification reaction which is carried out by acetic acid and isoamyl alcohol was investigated.

MATERIALS AND METHODS

Instrument and reagents

Way refractor (Shanghai, China), Y-4Q X-ray diffractometer (Dandong, China) and FTS-40 Fourier transform infra-red spectrometer (America Biorad) are used in this experiment.

Natural graphite (C, 5092) is provided by Action Carbon CO. LTD, Baoding, China. Acetic acid, Isoamyl alcohol, H₂SO₄ (96%-98%), KMnO₄, Na₂CO₃, CaCl₂, FeCl₃·6H₂O, Fe₂(SO₄)₃, NaCl are all analytical reagents.

Preparation of GIC_I with sulfuric acid and ferric chloride as intercalation reagent

Take FeCl₃·6H₂O with definite quality using beaker, and take a certain volume of sulfuric acid (diluted to the mass ration of 75%) to join the beaker, then add certain quality dry natural graphite and KMnO₄ in turn, mix the ingredients using glass rod, and reaction last out 1h at a certain temperature. The product is casted into dishes to be washed until pH equals 6.0~7.0, and then dried at 60 ~ 80°C, GIC_I is obtained.

Sift the product with standard sifter, weigh accurately about 0.3000g GIC_I, and then expand it at 900°C in Muffle to get expanded volume. In the preparation of GIC_I, the amount of natural graphite, H₂SO₄, FeCl₃·6H₂O and the density of H₂SO₄ has been listed in Table 1.

Preparation of GIC with sulfuric acid as intercalation reagent

Graphite intercalation compound is prepared with only H₂SO₄ as intercalation reagent, proportion of the reactants is C: KMnO₄: H₂SO₄ =1: 0.32: 3.8, H₂SO₄ is diluted to the mass ration of 75%, and the reaction is carried out at 25°C for 1h. The product is signed as GIC_{II}.

Characterization of graphite

To confirm whether the intercalation is successful or not, and to make preliminary analysis of the existing form of ferric compound in GIC_I, XRD analysis is applied to characterize the structure of the various graphite.

Synthesis of isoamyl acetate catalyzed by GIC_I

Add acetic acid and isoamyl alcohol (mol ratio 1.5:1.0) into reactor appending agitator and water separator, then add GIC_I (7.5% of gross mass of acetic acid and isoamyl alcohol). The reaction last 2.5h at boiling point, then filter the mixture to separate catalyst and the liquid product. Mix liquid product with saturated sodium carbonate solution, saturated sodium chloride solution, and saturated calcium chloride solution in turn, after demixion and separation with separating funnel, the organic layer is distilled at atmospheric, and the distillation of 134~141°C is collected. Esterification rate of acetic acid (limiting dosage factor) is calculated according to equation (1), and the product is detected with refractive index and IR.

$$\text{Esterification rate} = \frac{\text{mass of isoamyl acetate actually achieved}}{\text{mass of isoamyl acetate theoretical achieved}} \quad (1)$$

Table 1: Factors and level in the preparation of GIC_I *

Factors and Levels	KMnO ₄ :C g/g	H ₂ SO ₄ :C g/g	Temperature °C	FeCl ₃ :C g/g
1	0.32	3.8	25	0.13
2	0.34	3.9	32	0.15
3	0.36	4.0	42	0.17

* 1g natural graphite is set as benchmark.

RESULTS AND DISCUSSION

Results of the orthogonal test

According to the former research ^[10], the catalytic activity of GIC_{II} with sulfuric acid as the intercalation reagent is related to the quantity of intercalated sulfuric acid. The more sulfuric acid is inserted, the stronger the GIC_{II}'s acid property, the higher the catalytic activities and the bigger the expanded volume. We performed the orthogonal test according to Table 2, expanded volume (EV) of GIC_I and esterification rate of iso-amyl acetate are taken as the optimal object. We can conclude from Table 2 that the catalytic activity of GIC_I has no direct relationship with its expanded

volume, but the temperature has more obvious influence; the addition of FeCl₃ may reduce the total intercalation of sulfuric acid, which decreases the ultimate expanded volume. However, the intercalation of ferric compound may improve the catalytic activity of expansible graphite. With esterification rate as the priority object and sulfuric acid and FeCl₃ as intercalation reagents, the feasible method to prepare higher catalytic activity GIC_I is: C: KMnO₄:H₂SO₄: FeCl₃=1:0.32:3.8:0.15, and decision of reaction temperature needs a further experiment.

Table 2: L₉(3⁴) orthogonal experiment and results

Factors Number	KMnO ₄ :C g/g	H ₂ SO ₄ :C g/g	Temperature °C	FeCl ₃ :C g/g	EV mL/g	Esterification rate%
1	0.32	3.8	42	0.15	370	82.1
2	0.34	3.8	25	0.13	380	63.2
3	0.36	3.8	32	0.17	400	65.3
4	0.32	3.9	32	0.13	430	56.7
5	0.34	3.9	42	0.17	430	72.8
6	0.36	3.9	25	0.15	350	79.0
7	0.32	4.0	25	0.17	330	75.4
8	0.34	4.0	32	0.15	420	64.8
9	0.36	4.0	42	0.13	430	71.5
Sum _{level 1}	1130 (214.2)	1150 (210.6)	1060 (217.6)	1240 (191.4)		
Sum _{level 2}	1230 (200.8)	1210 (208.5)	1250 (186.8)	1140 (225.9)		
Sum _{level 3}	1180 (215.8)	1180 (211.7)	1230 (226.4)	1160 (213.5)		
R	100 (15)	60 (3.2)	190 (39.6)	100 (34.5)		

* In the experiment, 1g natural graphite is set as benchmark.

Range Analysis value of esterification rate is put in parenthesis.

The XRD analysis of graphite

In order to investigate whether the intercalation reaction is successful or not, the natural graphite and GIC₁ prepared under different conditions are analyzed with XRD. As showed in Fig.1 (a), 3.32 Å and 1.67 Å are the characteristic diffraction peaks of natural graphite. There are new diffraction peaks in both figure (b) and (c) of GIC₁ prepared under different conditions, which indicates the intercalation of new substance into the layers and the changes of crystal structure of natural graphite. Elemental analysis to the characteristic diffraction peaks of GIC₁ shows that iron exists in the form of Fe₂(SO₄)₃. Videlicet, in intercalation reaction of natural graphite with H₂SO₄ and FeCl₃ under the oxidation of KMnO₄, the final intercalation form of Fe³⁺ is Fe₂(SO₄)₃.

Influence of reaction temperature on GIC₁' catalytic activity

To investigate the feasible temperature, a series of single-factor experiments are carried out with mass ratio of C: KMnO₄:H₂SO₄: FeCl₃ equal to 1:0.32:3.8:0.15. Results show that we can get the highest esterification rate of 86.0% when the intercalation reaction temperature is control as 40°C (as showed in Fig. 2). Too low temperature would cause the inadequate intercalation of H₂SO₄ and FeCl₃; On the other hand, too high temperature would cause the excessive oxidation of graphite; these can all cause the decrease of GIC₁' catalytic activity. Among the tested range of 15~62°C the influence of reaction temperature on esterification rate is not obvious. Finally, in the preparation of GIC₁ with H₂SO₄ and FeCl₃ as intercalation reagent, room temperature is used.

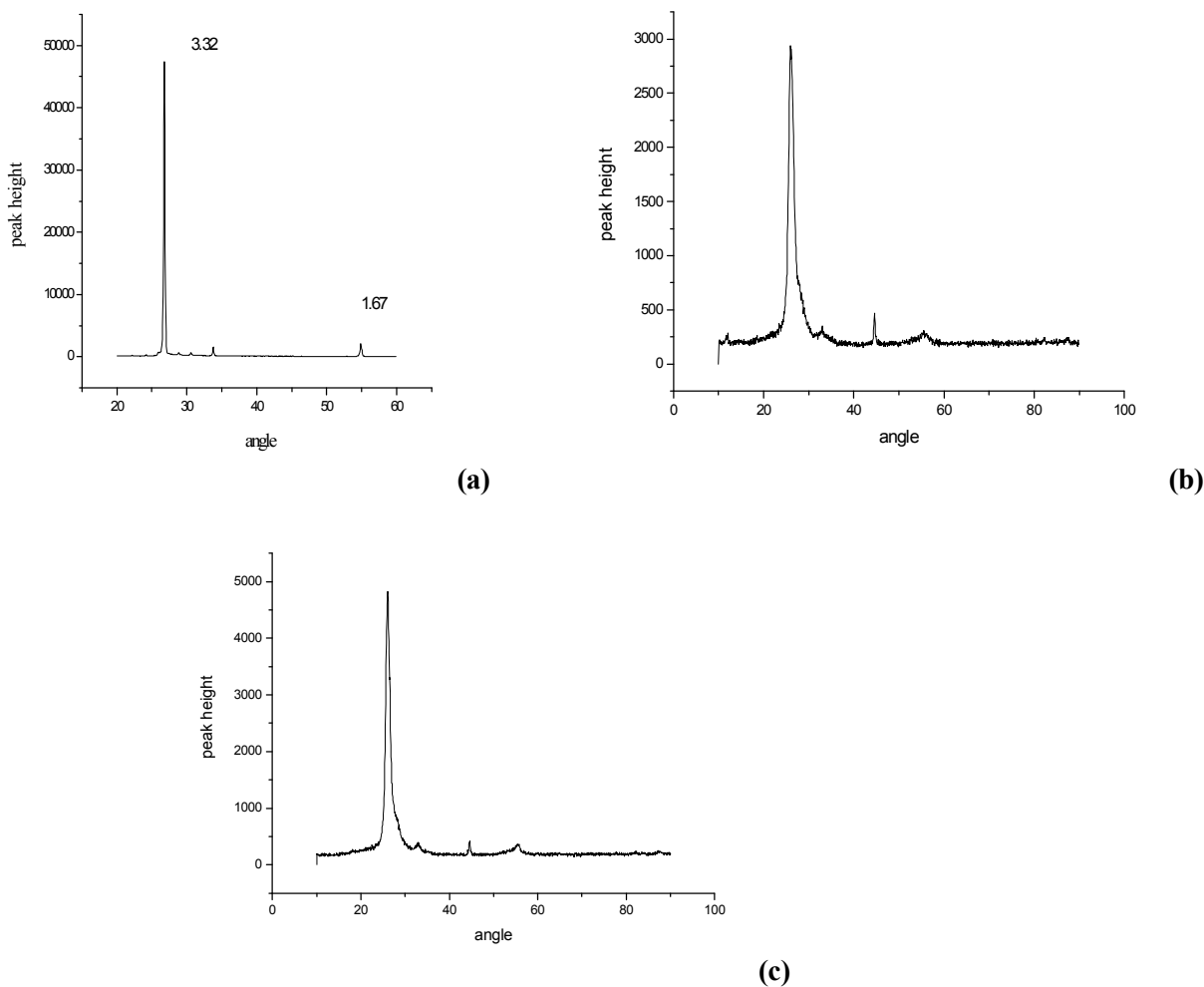


Fig. 1: XRD of natural graphite and GIC₁
(a) Natural graphite (b) GIC₁ with EV of 430mL/g, FeCl₃ 0.13g/g
(c) GIC₁ with EV of 330mL/g, FeCl₃ 0.17g/g

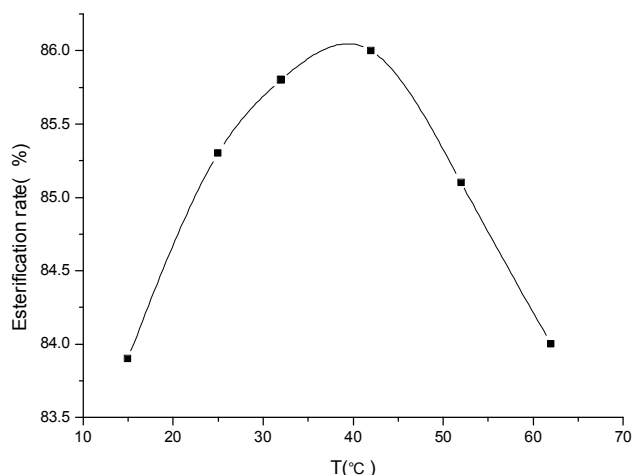


Fig. 2: Influence of intercalating reaction temperature on GIC_I' catalytic activity

Comparison of catalytic activity of different catalysts

To investigate catalytic activity of different esterification catalysts of H₂SO₄ with a mass concentration of 96%, Fe₂(SO₄)₃, FeCl₃·6H₂O, GIC_I and GIC_{II}, parallel experiments are carried out. The results listed in Table 3 illustrate Fe₂(SO₄)₃ and FeCl₃·6H₂O have the highest catalytic activity than other catalysts, but they can not be recycled after the reaction. Relatively, GIC_I possesses higher catalytic activity and it can be filtrated and recycle after reaction.

Study of recycling rate of GIC_I

The recycling experiment of GIC_I with H₂SO₄ and FeCl₃ as intercalation reagent indicates that the esterification rate for the first time is 86%, for the second time is 64%, and after the third time, it reduce

to 50%. These might be caused by the change of GIC_I' edge structure and increasing the mass transfer resistance between solid-liquor phases, which lead to a lower catalytic activity in a limited time.

Study of expanded volume of GIC_I after esterification reaction

After filtering and drying, the GIC_I who has been used as catalyst on synthesis of isoamyl acetate is expanded at 900°C. Comparison between the expanded volume before and after esterification reaction shows that it has little change (as listed in Table 4), and esterification reaction can not change the expanding capacity of GIC_I, GIC_I can be used for sealing material and adsorption material subsequently.

Table 3: Effect of different catalyst on esterification rate*

Catalysts	96%H ₂ SO ₄	GIC _I	GIC _{II}	Fe ₂ (SO ₄) ₃	FeCl ₃ ·6H ₂ O
Esterification rate /%	88.0	86.0	84.0	94.5	95.6

* GIC_I prepared with H₂SO₄ and FeCl₃·6H₂O as intercalation reagent.

GIC_{II} prepared with only H₂SO₄ as intercalation reagent.

Table 4: Comparison of expanded volume between GIC₁*

GIC ₁	EV before the catalytic	EV after the catalytic
	reaction (mL/g)	reaction (mL/g)
1	325	325
2	360	360
3	375	385
4	390	390
5	380	375
6	370	370

*GIC₁ 1~6 are prepared under different reaction temperature just the same as that showed in Fig. 2

CONCLUSIONS

In this experiment, GIC₁ is prepared with H₂SO₄ and FeCl₃ as intercalation reagent. The process combines the preparation of expandable graphite with the loading of ferric-doped. The influential factors on the catalytic activity of GIC₁ is defined as: C:KMnO₄:H₂SO₄(75%): FeCl₃=1:0.34:3.9(75%):0.15. GIC₁ with expanded volume of 420 mL/g and 86% yield of isoamyl acetate is prepared after reacting 60 minutes at room temperature. The research indicates

that GIC₁ show higher catalytic activity, and it is recycling and reusable.

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