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Preparation of Expandable Graphite and Its Catalysis Performance for the Synthesis of Isoamyl Acetate

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Five kinds of expandable graphite with different expanded volume and different intercalation compounds are produced. In order to testify the intercalation reaction in graphite, XRD analysis of natural graphite and expandable graphite are carried out. Its catalysis performance for the synthesis of isoamyl acetate is studied. The influence of molar ratio of isoamyl alcohol to acetic acid, amount of catalyst, reaction time, initial intercalation reagents of graphite on the yield of isoamyl acetate is examined in detail. The reusing capability of catalyst is also studied. We get the suitable conditions of the esterification as follows when tetrabutyltitanate is used as intercalation reagent of graphite: molar ratio of isoamyl alcohol to acetic acid equals to 1.5:1.0, mass of catalyst equals to 7.5 % of the total mass of reactants, reaction time is 2.5 h and temperature keeps at boiling point. The esterification rate of 87.9 % can be achieved. Expandable graphite prepared with different intercalation reagents has different catalytic activity, the one with tetrabutyltitanate as intercalation reagent has better catalysis activity for this esterification reaction, and its reuse rates are: 87.9 % for the first time, 63.8 % for the second time and 40.2 % for the third time. Results testify the expandable graphite has higher catalytic activity, short reaction time, easily being separated.

Key Words: Expandable graphite, Tetrabutyltitanate, Intercalation reagent, Isoamyl acetate, Catalytic activity.

INTRODUCTION

Expandable graphite is a kind of new material which can be prepared through intercalation reaction of H_2SO_4 and other intercalating reagents under the condition of chemical or electro-chemical oxidation[1,2]. Its application is normally focused on seal material or adsorbent after being expanded under high temperature[3,4]. At the same time, expandable graphite can be used as solid acid catalyst for its loading[5,6] to H^+.

Isoamyl acetate is one kind of flavour reagents with fruity smell. It is traditionally prepared with H_2SO_4 as catalyst[7]. The use of H_2SO_4 often causes the problems such as corrosion for equipments, difficult to be recycled and pollution for environment. Until now, the tried replacers include $FeCl_3$, $CuSO_4$, ferric tri-dodecane sulfonate, $FeCl_3/MnO_2$, KH_2PO_4, SO_4^{2-}/TiO_2-SiO_2, $TiSiW_{12}O_{40}/TiO_2$ and so on[8-14]. But some shortcomings limit theirs widely application in industry such as higher wastage for materials, lower yield of product or higher cost in catalyst preparation.

Expandable graphite can be prepared through one step reaction under gentle condition, lower cost and it can be easily dispersed and recycled. At the same, expandable graphite prepared with different intercalation reagent has different catalytic activity. Base on this reason, expandable graphite is prepared with five different methods and its catalysis for esterification reaction between acetic acid and isoamyl alcohol is studied. To improve the yield of isoamyl acetate, the influences of catalyst amount and its preparing method, materials ratio, reaction time on esterification reaction are investigated.

EXPERIMENTAL

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, H_2SO_4 (96-98 %), $KMnO_4$, $TiCl_4$, tetrabutyl titanate $C_{16}H_{36}O_4Ti$, $FeCl_3$, ferrocene $(C_5H_5)_2Fe$, Na_2CO_3, $CaCl_2$, NaCl are all analytical reagents.

Preparation of expandable graphite

Method I: Expandable graphite I is prepared with H_2SO_4 and $C_{16}H_{36}O_4Ti$ as intercalation reagent: Under 45 ºC, 4 g of natural graphite is mixed with 9 mL of H_2SO_4 (75 %) and 2.0 g $KMnO_4$ in a 250 mL beaker and 1.6 mL of $C_{16}H_{36}O_4Ti$ is added immediately under stirring condition. After 1 h, product is washed with deionized water until pH reaches to 6-7, then filtrated and dried at 75-80 ºC for about 3 h, expandable graphite I is obtained.

Method II: Expandable graphite II is prepared with H_2SO_4 and $TiCl_4$ as intercalation reagent: Under 45 ºC, 4 g of natural graphite is mixed with 9 mL of H_2SO_4 (75 %) and 2.0 g $KMnO_4$ in a 250 mL beaker and 0.8 mL of $TiCl_4$ is added immediately under stirring condition. After 1 h, product is washed with deionized water until pH reaches to 6-7, then filtrated and dried at 75-80 ºC for about 3 h, expandable graphite II is obtained.

Method III: Expandable graphite III is prepared with H_2SO_4 and $FeCl_3$ as intercalation reagent: Under 45 ºC, 4 g of natural graphite is mixed with 12 mL of H_2SO_4 (75 %) and 1.4 g $KMnO_4$ in a 250 mL beaker and 0.45 g of $FeCl_3$ is added immediately stirring condition. After 1 h, product is washed with deionized water until pH reaches to 6-7, then filtrated and dried at 75-80 ºC for about 3 h, expandable graphite III is obtained.

Method IV: Expandable graphite IV is prepared with H_2SO_4 and $(C_5H_5)_2Fe$ as intercalation reagent: Under 45 ºC, 4 g of natural graphite is mixed with 12 mL of H_2SO_4 (75 %) and 2.4 g $KMnO_4$ in a 250 mL beaker and 0.45 g of $(C_5H_5)_2Fe$ is added immediately stirring condition. After 1 h, product is washed with deionized water until pH reaches to 6-7, then filtrated and dried at 75-80 ºC for about 3 h, expandable graphite IV is obtained.

Method V: Expandable graphite V is prepared with H_2SO_4 as intercalation reagent: Under 45 ºC, 4 g of natural graphite is mixed with 9 mL of H_2SO_4 (75 %) and 2.0 g $KMnO_4$ in a 250 mL beaker. After 1 h, product is washed with deionized water until pH reaches to 6-7, then filtrated and dried at 75-80 ºC for about 3 h, expandable graphite V is obtained.

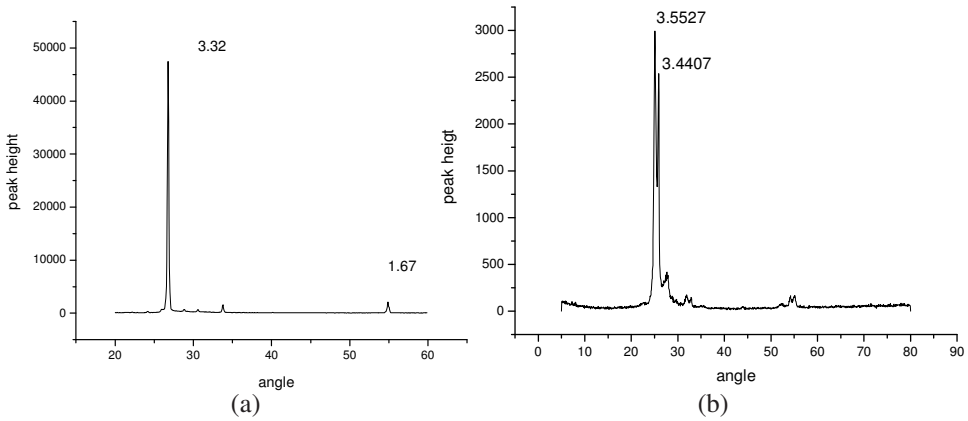
Preparation of isoamyl acetate: At a definite mole ratio, acetic acid and isoamyl alcohol are added into the reactor appending stirrer and water segregator. Reaction lasts a certain time under the catalysis of expandable graphite prepared above. Then the products are deal with filtration under vacuum, wash with saturated solution of Na_2CO_3, $CaCl_2$ and NaCl, respectively. The upper layer solution is deal with distillation under air pressure, fraction corresponding to 138-142 ºC is collected. The distillate is analyzed with refractor and IR, respectively and yield of isoamyl acetate is calculated according to eqn. 1.

$$\text{Yield (\%)} = (m_{\text{obtained isoamyl acetate}}/m_{\text{theoretical isoamyl acetate}}) \times 100\ \% \quad (1)$$

RESULTS AND DISCUSSION

Analysis of expandable graphite

XRD of natural graphite and expandable graphite: To testify intercalation reaction and the form of intercalation compounds, natural graphite and those prepared expandable graphite are analyzed with XRD. As showed in Fig. 1, main diffraction peaks of expandable graphite are different from that of natural graphite, which testify the change of crystal structure and the existence of intercalation reaction. At the same time, compared these spectra with the known standard substance, it is presumed that titanium exists in the form of $Ti(SO_4)_2$ or anatase TiO_2 in expandable graphite I and II, iron exists in the form of $Fe_2(SO_4)_3$ in expandable graphite III and IV. In spectrum of expandable graphite V, the characteristic speak of SO_2 is observed. So expandable graphite can load solid acid through intercalation of reagent in graphite and it can be called as solid acid catalyst.



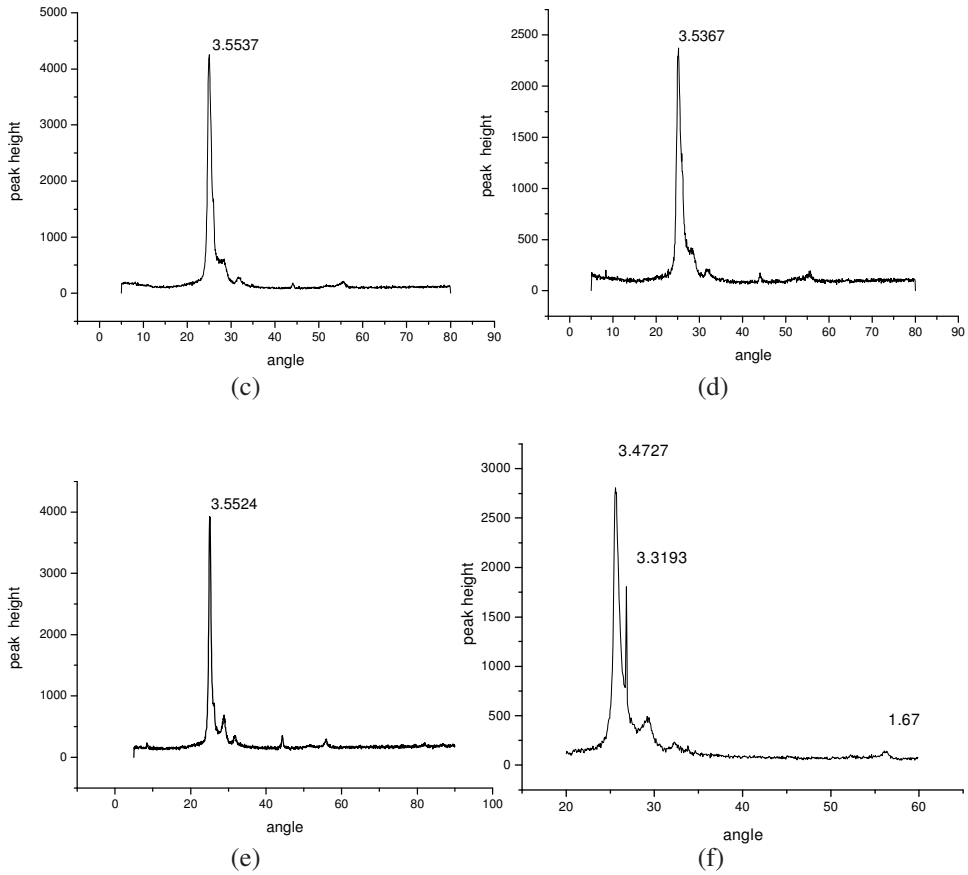


Fig. 1. XRD of natural graphite and expandable graphite: (a) natural graphite, (b) expandable graphite I, (c) expandable graphite II, (d) expandable graphite III, (e) expandable graphite IV, (f) expandable graphite V

Expanded volume (EV) of expandable graphite: 0.300 g expandable graphite prepared with different method is expanded instantly at 900 ºC and the volume of product is detected with measuring cup. Expanded volume is defined as the volume of expanded graphite corresponding to 1.0 g of expandable graphite, as mL g^{-1}. Results listed in Table-1 testify the intercalation reaction and the formation of new intercalation compounds. Expandable graphite prepared with different method has different expanded capability.

Optimizing of esterification reaction: With expandable graphite I as catalyst, the influences of catalyst amount, mole ratio of isoamyl alcohol to acetic acid, reaction time on yield of isoamyl acetate are studied through single factor and multi-factor $L_9(3^4)$ orthogonal experiment. Optimum conditions are gained as: *n*(isoamyl alcohol):*n*(acetic acid) = 1.5:1.0, *w*(expandable graphite I) = 7.5 % total amount of materials, reaction time 2.5 h and temperature keeping at boiling point. Yield of isoamyl acetate is 87.9 %.

TABLE-1
EXPANDED VOLUME OF EXPANDABLE GRAPHITE

Exp. graphite	I	II	III	IV	V
Intercal. reagent	$H_2SO_4 + C_{16}H_{36}O_4Ti$	H_2SO_4+ $TiCl_4$	H_2SO_4+ $FeCl_3$	H_2SO_4+$(C_5H_5)_2Fe$	H_2SO_4
EV (mL g^{-1})	360	340	340	330	340

Influence of mole ratio between isoamyl alcohol and acetic acid on yield: During the esterification, isoamyl alcohol plays the role of dehydrolyzing agent, so that the ratio of alcohol and acetic acid larger than 1.0 is investigated. As showed in Fig. 2, yield of isoamyl acetate increases with the increase of ratio when the value is smaller than 1.5. But when it exceeds 1.5, yield begins to decrease. Too high dosage of isoamyl alcohol can increase wastage of heat and debase purity of product. So the optimum ratio of alcohol to acid is detected as 1.5:1.0.

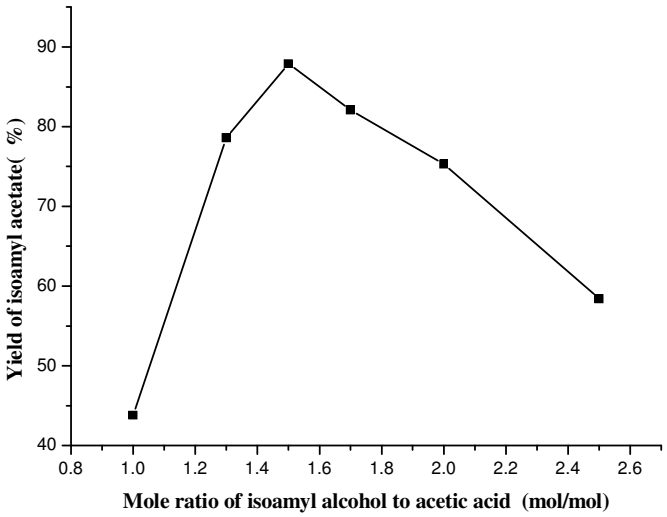


Fig. 2. Influence of alcohol/acid mole ratio on isoamyl acetate yield

Influence of catalyst dosage on yield: Yield of isomyl acetate increases slowly with the increase of catalyst dosages in the range of 2.5-7.5 %. To keep low cost, the dosage of catalyst can be fixed as 7.5 % of total mass of isoamyl alcohol and acetic acid.

Influence of reaction time on yield: In the range of 1.5-2.5 h, yield of isomyl acetate increases slowly and influence of reaction time is not obvious. It is confirmed as 2.5 h.

Comparison of catalysis activity of expandable graphite: As proved that expandable graphite prepared with different intercalation reagent possess different intercalation compound and different expanded volume. Their catalysis activities for esterification reaction of isoamyl alcohol and acetic acid are investigated under the condition of: *n*(isoamyl alcohol):*n*(acetic acid) = 1.5:1.0, *w*(expandable graphite)

= 7.5 % total amount of materials, reaction time 2.5 h and temperature keeping at the boiling point. As showed in Table-2, different intercalation reagents in graphite cause different strength of solid acid, then cause different catalysis activity and isoamyl acetate yields. Expandable graphite I shows higher activity than other tested solid acids.

TABLE-2
COMPARISON OF CATALYTIC ACTIVITY

Catalyst	expandable graphite I	expandable graphite II	expandable graphite III	expandable graphite IV	expandable graphite V	H_2SO_4 (96-98 %)
Intercalation reagent	H_2SO_4 + $C_{16}H_{36}O_4Ti$	H_2SO_4 + $TiCl_4$	H_2SO_4 + $FeCl_3$	H_2SO_4 + $(C_5H_5)_2Fe$	H_2SO_4	–
Yield of isoamyl acetate (%)	87.9	72.3	63.8	75.3	50.2	92.8

Reuse of expandable graphite: Expandable graphite I shows better activity for the proposed esterification reaction, so its reuse is carried out under the mentioned optimum esterification condition. Before reuse, the catalyst is treated with filtration and dried at 75-80 ºC. Its reuse rates are: 87.9 % for the first time, 63.8 % for the second time and 40.2 % for the third time. The decrease of reuse rate may be caused by the change of brim structure of expandable graphite grain, which may increase the mass transfer resistance. But the expanded volume of this reused catalyst is just the same as that of its initial expanded volume. It can be recycled as catalyst, seal material and adsorbent.

Conclusion

Expandable graphite shows higher catalytic activity for esterification of isoamyl alcohol and acetic acid. Expandable graphite prepared with different intercalation reagent in graphite has different catalytic capability.

With expandable graphite I as catalyst, the optimum esterification conditions are gained as: *n*(isoamyl alcohol):*n*(acetic acid) = 1.5:1.0, *w*(expandable graphite I) = 7.5 % total amount of materials, reaction time 2.5 h and temperature keeping at boiling point. Yield of isoamyl acetate is 87.9 %.

As a catalyst of esterification, expandable graphite possesses of characteristics of easy preparation, easy decentralization in reaction system, easy separation and smaller mole ratio of isoamyl alcohol to acetic acid, shorter reaction time and higher yield. As one kind of solid acid catalyst, expandable graphite can be used in organic reaction which has proton transfer.

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