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Catalytic activity of expansible graphite for the synthesis of Propyl acetate

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Abstract: The catalysis of expandable graphite EG for esterification has been studied.EG was prepared with KMnO4 as oxidant and $H_2S\ O_4$ as inserting reagent. Expanded volume ,X-ray diffraction and energy dispersive analysis for EG were carried, and its catalytic activity was detected in the reaction of acetic acid with propanol. Influence of mole ratio of propanol and acetic acid, dosage of EG, reaction time on ester yield were optimumed through orthogonal experiments and single factor experiments. The suitable esterification condition is: molar ratio of propanol to acetic acid keeps 2.0 : 1.0, mass of EG keeps 8.0 % of the total mass of reactants, reaction keeping up 0.5 h ~ 1.0 h and temperature keeps at the boling point, and esterification rate of 96.0 % can be achieved. The reuse ester yield is 75 % for first reuse and 60 % for the second reuse.

Key words：Expandable graphite, Propyl acetate, Catalytic activity, Reuse.

INTRODUCTION

Expandable graphite EG is a kind of new material which is prepared through intercalation reaction of non-carbon substance such as H_2SO_4 under the condition of chemical or electric chemistry oxidation [1, 2]. Its is normally used as sealing material and adsorbent of oil after being expanded under high temperature [3, 4]. At the same time, EG can be used as solid super acid catalyst in acylation reaction [5, 6].

As a kind of flavour reagent with fruit taste, propyl acetate has been widely used in food machining, printing, and it is called as "all-purpose solvent" for its excellent solubility for many organic reagent. In the synthesis of propyl acetate, H_2SO_4 is the traditionary catalyst, and the use of H_2SO_4 often causes problems such as equipment corrosion and environment pollution. Now, the tested replacers are $Al_2(SO_4)_3$, Ionic Liquid, Ionic exchange resins, H_2SO_4 or sulfates supported by porous carrier, Heteropolyacid, $TiSiW_{12}O_{40}/TiO_2$ and so on [7-13]. But some shortcomings limit theirs application in industry such as higher wastage for reactants, lower yield of ester (among 70% ~ 97%) or high cost in catalyst preparation.

EG has the advantages of being easy prepared, lower cost, easy dispersed and can be recycled and used as sealing material or adsorbent. Base on this reason, the catalysis of EG for esterification between acetic acid and propanol was studied. The influences of catalyst amount, materials ratio, reaction time on ester yield were investigated.

MATERIALS AND METHODS

SX3-4-13 Muffle furnace (Tientsin,precision of temperature ±0.1% -0.4% °C), WAY refractor (Shanghai,China), Y-4Q X-ray diffractometer (Dandong,China), Energy dispersive spectrum instrument EDS (Therom NORAN Vantage DIS) and FTS-40 Fourier transform infra-red spectrometer (America Biored) were used in this experiment.

Natural graphite (**C**, 5092) was provided by Action Carbon CO. LTD, Baoding, China. Acetic acid, propanol, H_2SO_4 (96%), $KMnO_4$, Na_2CO_3, $CaCl_2$, NaCl are all analytical reagents.

Preparation of EG

At 30°C ,3.0 g of natural graphite is mixed with 13.0 Ml of H_2SO_4 (mass concentration 75%) and 0.45 g KMnO4 in a 250 Ml beaker.After 30 min.,product is washed with de-ionized water until Ph reaches to 60. ~ 7.0, and then diped in de-ionized water for 2.0 h.Through filtration and dryness at 75-80°C for about 3h,EG is gained.

Character of EG

Expanded volume (EV) of EG

EV is and important factor to judge of the interacalation reaction of H_2SO_4 into graphite.0.300 g EG is expanded instantly at 900°C and turn into expanded graphite, and the volume of product is detected with a measuring cup.EV is defined as the volume of expanded graphite corresponding to 1.0 gram of EG writted as Ml/g and it is detected as 416 Ml/g.

X-ray spectrum of material graphite and EG

Analysis of XRD for material graphite and EG were carried out. The two peaks of 3.34 Å and 1.67 Å are the characteristic spectrum of material graphite **(Fig. 1).** Because graphite has plane structure of samdwich, the peak of 3.34 Å is strengthened during XRD detection. In the XRD analysis of EG (**Fig. 2),** the characteristic peak of 3.34 Å is replaced with a new peak of 3.42 Å. The displacement of diffraction peak to big angle show the layer space is bigger than the material graphite, and new substance has inserted into samdwich. The lager EV expandable graphite possessed, the higher dosage of H_2SO_4 it would hold[14].

EDS analysis of EG

Fig. 3 and 4 are results of EDS for material graphite and EG. It gives a relative higher intensity of S element in EG'EDS than that of material graphite, which testifies the intercalaction of H_2SO_4 [14].

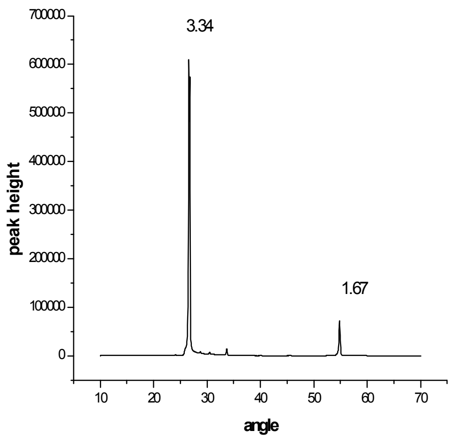

Fig. 1: XRD of material graphite

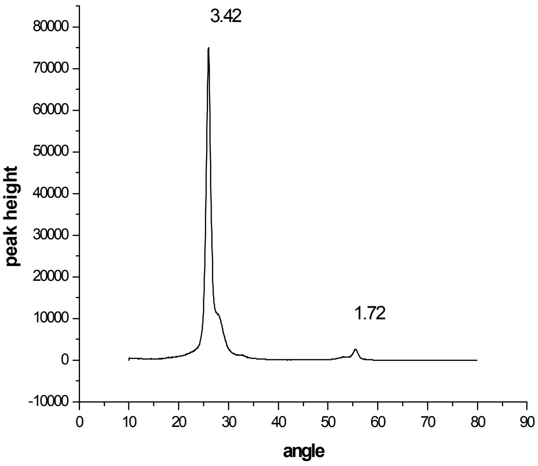

Fig. 2: XRD of EG

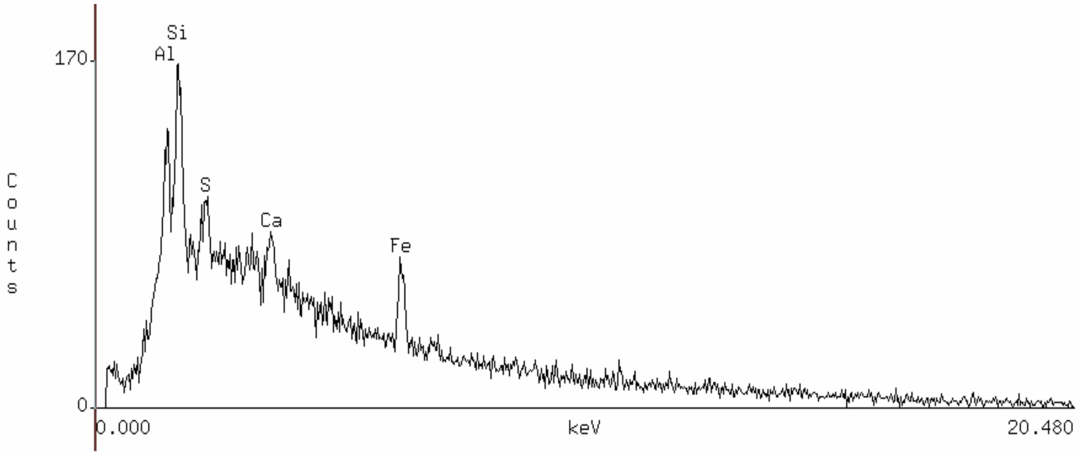

Fig. 3: EDS of material graphite

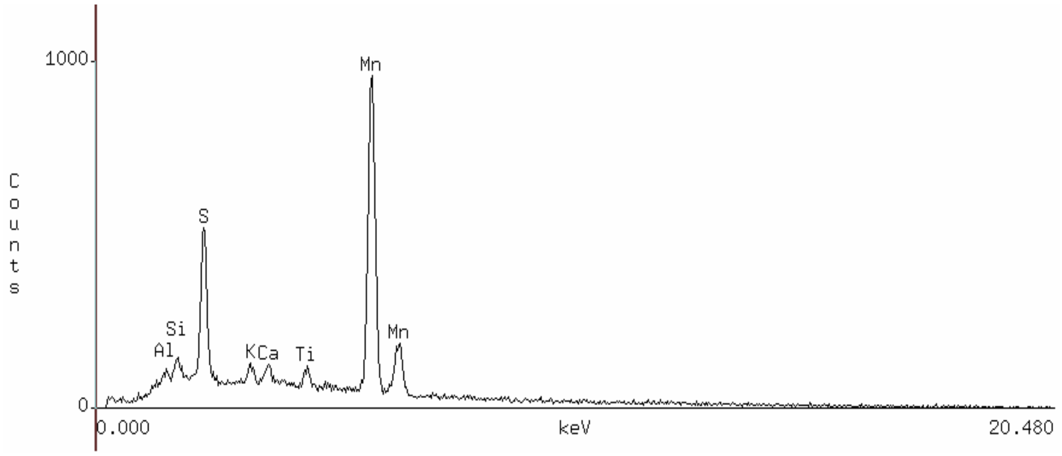

Fig. 4: EDS of EG

Preparation of propyl acetate

At a definite mole ratio, acetic acid and propanol are added into the reactor appending stirrer and water segregator. Reaction lasts a certain time under the catalysis of EG. Then the products are filtrated under vacuum, washed with saturated solution of Na_2CO_3, $CaCl_2$ and NaCl, respectively. The upper layer solution is distilled under air pressure, the fraction corresponding to 92 ~ 98 °C is collected. Then distillate is analysed with refractor and IR, respectively. The collected product in distillation is colorless, transparent and with the taste of fruit. Its refractive index is detected as 1.3835 at 25 °C (reported value 1.383 ~1.385). In the IR spectrum analysis of the distillate, characteristic peak of C-H (2952.67 cm^{-1}), C-C(=O)-O (1178.29 cm^{-1}) are all observed. Yield of propyl acetate is calculated according to equation (1).

$$\text{Yield\%} = (m_{\text{obtained propyl acetate}} / m_{\text{theory propyl acetate}})*100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Table 1: Results of $L_9(3^4)$ experiment for the synthesis of propyl acetate

Factor /Sample	n(propanol): n(acetic acid)	*w* (catalyst) /%	Reaction time /h	Yield of propyl acetate /%
1	2.0:1.0	10	2.0	90.05
2	2.0:1.0	8	1.5	93.78
3	2.0:1.0	6	1.0	86.88
4	1.8:1.0	10	1.0	85.10
5	1.8:1.0	8	2.0	79.76
6	1.8:1.0	6	1.5	88.09
7	1.5:1.0	10	1.5	68.69
8	1.5:1.0	8	1.0	81.80
9	1.5:1.0	6	2.0	66.21
$Sum_{level\ 1}$	270.71	243.84	253.78	1+2+3=740.36
$Sum_{level\ 2}$	252.95	255.34	250.56	
$Sum_{level\ 3}$	216.70	241.18	236.02	
R	54.01	14.16	17.76	

RESULTS AND DISCUSSION

Optimizing of esterification reaction

Influences of catalyst mass, mole ratio of propanol to acetic acid and reaction time on ester yield are studied through multi-factor $L_9(3^4)$ **experiment (Table 1).**

Influence of mole ratio between propanol and acetic acid on yield

Results showed in Table 1 show that mole ratio of propanol to acetic acid is the most important influence factor on

Propyl acetate yield, and it increase with the increase of propanol.To find the feasible valus,with mass of EG is set as 8.0% of the total mass of reactants, reaction keeps up 1.0h,1.8:1.0~ 2.2:1.0 is tested.As showed in Fig.5, the yield increased with the increase of propanol when the ratio is smaller than 2.0 : 1.0, beyond this value, the yield began to decrease. To high dosage of propanol would increase the wastage of heat, and debase the purity of product. So the *n*(propanol) : *n*(acetic acid) = 2.0 : 1.0 should be used.

Influence of catalyst dosage on yield

As tested in $L_9(3^4)$ experiments, when the mass of EG is changed in the range of 6.0 % ~ 10.0% of the total mass of reactants, ester yield increases slowly. To decrease the wastage, it could be fixed as 8.0 % of the total propanol and acetic acid mass.

Influence of reaction time on yield

As listed in Table1,the yield decreases slowly with the increase of reaction time ranging from 1.0 h to 2.0 h.With mass of EG setting 8.0% of the total mass of reactants, ratio of n(propanol) : n(acetic acid) equals 2.0:1.0,the reaction tie in the range of 20~90 min are tested. Results showed in **Fig 6** give the feasible value is among 0.5 h to 1.0 h.

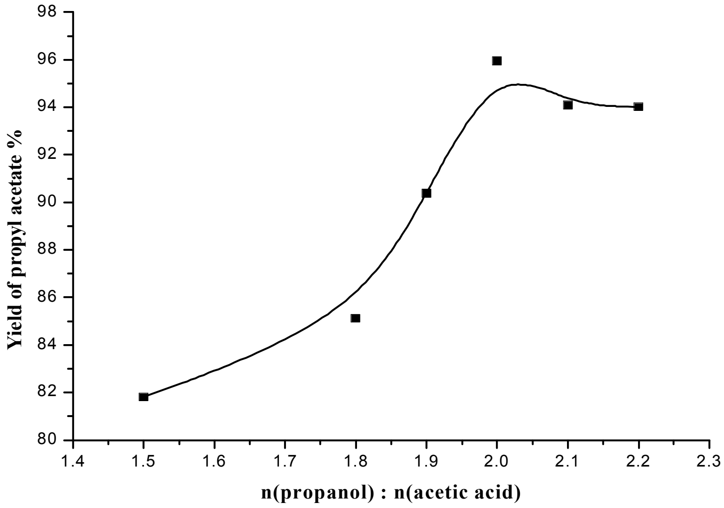

Fig. 5: Influence of propanol/acid mole ratio on ester yield

Condition：mass of EG is 8.0 % of the total mass of reactants，reactionkeeping up 1.0 h）

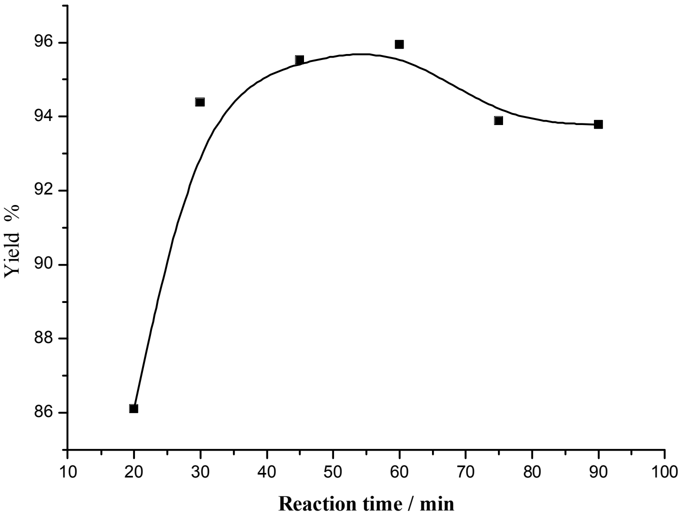

Fig. 6: Influence of reaction time on esterification conversion

(Condition：mass of EG is 8.0 % of the total mass of reactants，

ratio of *n*(propanol) : *n*(acetic acid) equals 2.0 : 1.0)

Table 2: EV of EG and reused EG

Using ime	1	2	3
EV mL/g	416	410	413

Selection of water-carrying agent

Function of water-carrying agent is increase the yield of ester through formation of azeotrope with water, which is in favor of the separation of water. The normally used water-carrying agent is cyclohexane, and the boiling point of azeotrope composed 8.4% water and 91.6% yclohexane is 68.95 °C [15]. Too low temperature would decrease reaction rate, and at the same time, the addition of too many of cyclohexane would consume a large amount of heat energy. When *n*(propanol) : *n*(acetic acid) = 2.0 : 1.0 is adopted, the superfluous propanol would play the role of carrying water. So no additional dehydrolyzing agent is needed.

Feasible condition to prepare propyl acetate with EG as catalyst

According to the $L_9(3^4)$ experiments and single factor experiments, the feasible conditions to get propyl acetate are gained as: *n*(propanol) : *n*(acetic acid) = 2.0 : 1.0, *w*(catalyst with a EV of 416 mL/g)=8.0% total amount of reactants, reaction keeping up 0.5 ~ 1.0 h, and temperature keeping at the boiling point. Yield of propyl acetate can reach 96.0%.

Reuse of EG

EG shows better activity for the aimed esterification reaction, so its reuse is carried out under the mentioned optimum esterification condition.Before reuse, the catalyst is treated with filtration and dryness under 75~ 80°C.Its reuse rates are 75% for the first time and 60% for the second time.The fall of reuse rate may be caused by the change of brim structure of EG grain, which may increase the mass transfer resistance. But the EV of this reused catalyst is just the same as that of its initial value **(Table 2).**

CONCLUSIONS

Through orthogonal experiments and single factor experiments, the feasible conditions to prepare propyl acetate are gained as: *n*(propanol) : *n*(acetic acid)= 2.0 : 1.0, *w*(EG with a EV of 416 mL/g) = 8.0% of the total amount of reactants, reaction keeping up 0.5 ~ 1.0 h and temperature keeping at the boiling point. Yield of propyl acetate can reach 96.0%.

EG possesses higher catalytic activity in esterification of propanol with acetic acid, and it could be used as polyphase catalyst in organic reaction with proton transfer.

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