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# Estrification of Acetic Acid with Isoamyl Alcohol over Expandable Graphite Catalyst

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**Abstract:** The catalysis of expandable graphite for esterification of acetic acid with isoamyl alcohol has been studied. Expandable graphite was prepared with three different methods. In esterification reaction, the influences of catalyst amount, materials ratio, reaction time, prepared method of the expandable graphite on esterification reaction were discussed. X-ray diffraction spectrum of expandable graphite testified the existence of  $\text{H}_2\text{SO}_4$  intercalation reaction. Through  $L_9(3^4)$  orthogonal experiment, optimum esterification reaction conditions were gained as:  $n(\text{isoamyl alcohol}):n(\text{acetic acid})=1.5:1$ ,  $w(\text{catalyst with a expandable volume of } 290 \text{ mL}\cdot\text{g}^{-1}) = 7.5\%$  total amount of materials, reaction time 1.5 h, and temperature keeping at the boiling point. Yield of isoamyl acetate reaches 96.0%. It was testified that expandable graphite was a kind of effective catalyst in the esterification of acetic acid with isoamyl alcohol.

**Keywords:** Expandable graphite; Catalysis; Isoamyl acetate; Esterification; Orthogonal experiment

## Introduction

Expandable graphite is a kind of new material which is prepared through intercalation reaction of  $\text{H}_2\text{SO}_4$  under the condition of chemical or electric chemistry oxidation<sup>1,2</sup>. Its application is normally focused on sealing material, adsorbent of oil, after being expanded under high temperature<sup>3,4</sup>. At the same time, expandable graphite can be used as solid super acid catalyst<sup>5,6</sup> for its loading to  $\text{H}^+$ .

Isoamyl acetate is a kind of flavour reagent with fruit taste. It is traditionally prepared with  $\text{H}_2\text{SO}_4$  as catalyst<sup>7</sup>. The use of  $\text{H}_2\text{SO}_4$  often causes the problems such as corrosion for

equipments and pollution for environment. Until now, the tried replaces include  $\text{FeCl}_3$ ,  $\text{CuSO}_4$ , ferric tri-dodecane sulfonate,  $\text{FeCl}_3/\text{MnO}_2$ ,  $\text{KH}_2\text{PO}_4$ , sulfonated polystyrene,  $\text{TiSiW}_{12}\text{O}_{40}/\text{TiO}_2$  and so on<sup>8-14</sup>. But some shortcomings limit them being widely applied in industry such as higher wastage for materials, lower yield of product or higher cost in catalyst preparation.

Expandable graphite possesses the characteristics of simple preparing process, lower cost, easy dispersed and can be recycled for further use such as sealing material or adsorbent. Based on this reason, the catalysis of expandable graphite to esterification reaction between acetic acid and isoamyl alcohol is studied. The influences of catalyst amount and its preparing method, materials ratio, reaction time on esterification reaction were investigated.

## Experimental

### *Instruments and reagents*

WAY refractor (Shanghai, China), Y-4Q X-ray diffractometer (Dandong, China) and FTS-40 Fourier transform infra-red spectrometer (America Biorad) were used in this experiment. Natural graphite (C, 5092) was provided by Action Carbon Co. Ltd, Baoding, China. Acetic acid, isoamyl alcohol,  $\text{H}_2\text{SO}_4$  (96%),  $\text{H}_2\text{O}_2$  (26%),  $\text{KMnO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCl}_2$ ,  $\text{NaCl}$  were all analytical reagents.

### *Preparation of expandable graphite*

#### *Method I*

At room temperature, 4.0 g of natural graphite was mixed with 10.6 mL of 96%  $\text{H}_2\text{SO}_4$  in a beaker, then 5.2 mL of 26%  $\text{H}_2\text{O}_2$  was added under stirring. After 30 min, products were washed with de-ionized water until pH reached to 6.0 ~ 7.0, then dried at 40~60 °C and expandable graphite could be gained.

#### *Method II*

At room temperature, 4.0 g of natural graphite was mixed with 6.5 mL of 96%  $\text{H}_2\text{SO}_4$  in a beaker, then 0.441 g of  $\text{KMnO}_4$  was added under stirring. After 30 min, products were washed with de-ionized water until pH reached to 6.0 ~ 7.0, then dried at 60 °C and expandable graphite could be gained.

#### *Method III*

At room temperature, 4.0 g of natural graphite was mixed with 7.5 mL of 96%  $\text{H}_2\text{SO}_4$  in a beaker, then 0.441 g of  $\text{KMnO}_4$  was added under stirring. After 30min, products were dipped in 10.0 mL of 4%  $\text{H}_2\text{O}_2$  water solution for 15 min, and washed with de-ionized water until pH reached to 6.0 ~ 7.0, then dried at 60 °C and expandable graphite could be gained.

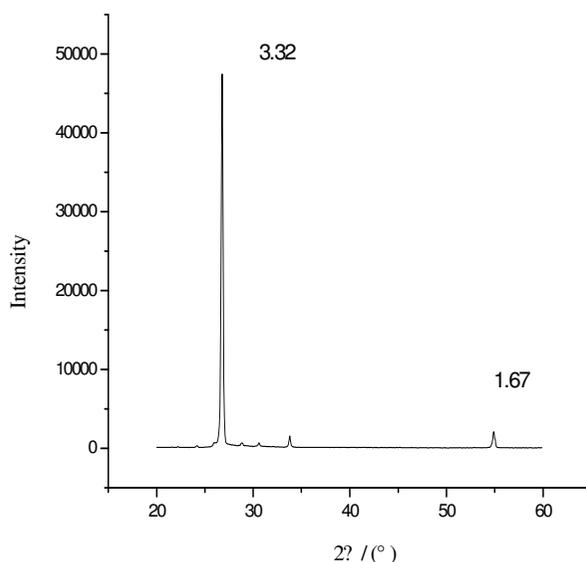
### *Preparation of isoamyl acetate*

At a definite mole ratio, acetic acid and isoamyl alcohol were added into the reactor appending stirrer and water segregator. The reaction lasted a certain time under the catalysis of expandable graphite. Then the products were deal with filtration under vacuum, washed with saturated solution of  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCl}_2$  and  $\text{NaCl}$ , respectively. The upper layer solution was deal with distillation under air pressure, the fraction corresponding to 138~142 °C was collected. The distillate was analysed with refractor and IR, respectively, and yield of isoamyl acetate was calculated.

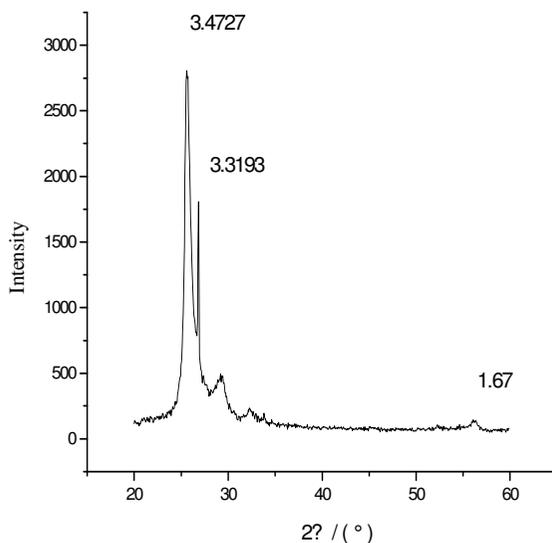
## Results and Discussion

### *Analyses of expandable graphite*

To testify the intercalation reaction of  $H_2SO_4$ , natural graphite and expandable graphite were analysed with X-ray diffractometer. As showed in Figure 1, 0.332 nm and 0.167 nm were two characteristic peaks of natural expanded. Figure 2 was the diffraction spectrum of expandable graphite. Besides the remained characteristic peak 0.332 nm of natural expanded, a new diffraction peak of 0.347 nm appeared, which testified the change of crystal structure and the existence of intercalation reaction.



**Figure 1.** The X-ray diffraction spectrum of natural graphite



**Figure 2.** The X-ray diffraction spectrum of expandable graphite

*The expanded volume (EV) of expandable graphite*

Expandable graphite prepared with different method would contain different dosage of  $\text{H}_2\text{SO}_4$ , this could be testified by EV of expandable graphite possessed. EV was detected<sup>15</sup> under 900 °C, and the results were listed in Table 1. The lager EV expandable graphite possessed, the higher dosage of  $\text{H}_2\text{SO}_4$  it would hold.

**Table 1.** EV of expandable graphite prepared with different method

Expandable graphite EV, $\text{mL}\cdot\text{g}^{-1}$	Method I	Method II	Method III
	180	280	290

*Optimizing of esterification reaction*

The influences of catalyst amount, mole ratio of isoamyl alcohol to acetic acid, reaction time, EV of the expandable graphite on esterification reaction were studied through single factor and multi-factor  $L_9(3^4)$  orthogonal experiment (Table 2). Optimum condition were gained as:  $n(\text{isoamyl alcohol}):n(\text{acetic acid})=1.5:1$ ,  $w$  (catalyst with a expandable volume of  $290 \text{ mL}\cdot\text{g}^{-1}$ )= $7.5\%$  total amount of materials, reaction time 1.5 h, and temperature keeping at the boiling point. Yield of isoamyl acetate reached 96.0%.

*Influence of mole ratio between isoamyl alcohol and acetic acid on yield*

To find the condign mole ratio between isoamyl alcohol and acetic acid, the ratio of isoamyl alcohol ranged from 0.4 to 0.7 was tested. As showed in Figure 3, the yield of isoamyl acetate increased with the ratio of isoamyl alcohol when the ratio was smaller than 0.6. But when it exceeded 0.6, the yield began to decrease. To high dosage of isoamyl alcohol would increase the wastage of heat, and debase the purity of product. So the optimum value of 0.6, namely,  $n(\text{isoamyl alcohol}):n(\text{acetic acid})=1.5:1$  should be used.

**Table 2.** Results of orthogonal experiment  $L_9(3^4)$  for the synthesis of isoamyl acetate

Number	$n(\text{isoamyl alcohol}):n(\text{acetic acid})$	$w$ (catalyst) %	Reaction time h	Yield of isoamyl acetate %
1	1.5:1.0	2.5	2.5	80.0
2	1.0:1.0	2.5	1.5	73.1
3	1.0:1.5	2.5	2.0	46.3
4	1.5:1.0	5.0	2.0	85.0
5	1.0:1.0	5.0	2.5	69.2
6	1.0:1.5	5.0	1.5	46.3
7	1.5:1.0	7.5	1.5	96.0
8	1.0:1.0	7.5	2.0	63.5
9	1.0:1.5	7.5	2.5	64.9

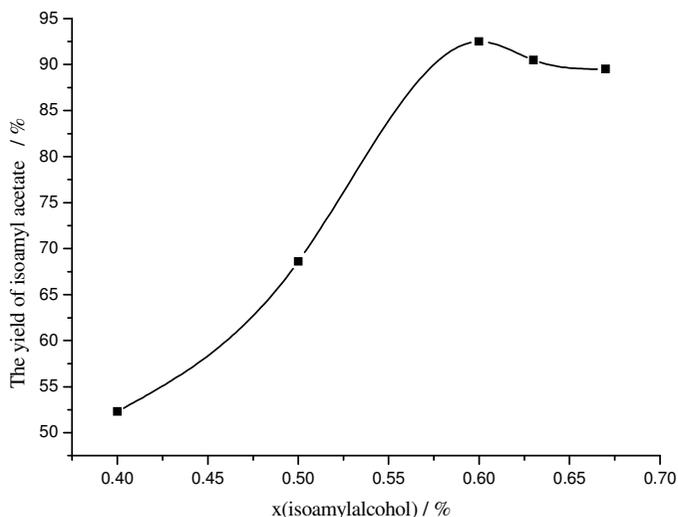
*Influence of catalyst dosage on yield*

In the range of  $2.5\% \sim 7.5\%$  catalyst dosages, yield increased slowly with the amount of expandable graphite. To keep low cost, the dosage of catalyst could be fixed as  $7.5\%$  of total isoamyl alcohol and acetic acid mass.

*Influence of preparing method of expandable graphite on isoamyl acetate yield*

In esterification reaction, expandable graphite could transfer proton and accelerate reaction rate. Expandable graphite, prepared with different method, should possess different EV and different dosage of  $\text{H}_2\text{SO}_4$ , and then it should have different catalyzing activity. Under the optimum technical condition as mentioned above, the catalyzing capability of these catalysts

was tested. From the results listed in Table 3, we could deduce that the higher EV the catalyst possessed, the higher catalyzing activity it should have, and the higher yield of isoamyl acetate should be obtained.



**Figure 3.** Influence of alcohol/acid mole ratio on esterification conversion (Condition: dosage of expandable graphite (EV=290 mL·g<sup>-1</sup>) equal 7.5%, reaction time 1.5 h)

**Table 3.** Influence of EV of expandable graphite on esterification\*

EV of expandable graphite possessed, mL·g <sup>-1</sup>	180	280	290
Yield of isoamyl acetate, %	80.0	90.0	96.0

\*Condition:  $n(\text{isoamyl alcohol}):n(\text{acetic acid})=1.5:1$ ,  $w(\text{catalyst})=7.5\%$ , reaction time 1.5 h

#### *Influence of reaction time on yield*

In the range of 1.5~2.5 h, the influence of reaction time on yield was very small. To insure the throughput, 1.5 h was used.

#### *Selection of dehydrolyzing agent*

When the mole ratio of  $n(\text{isoamyl alcohol}) : n(\text{acetic acid})=1.5:1$  was adopted, the superfluous isoamyl alcohol would play the role of removing water produced in the reaction. At the same time, isoamyl alcohol collected by water segregator could be reused. So, no additional dehydrolyzing agent needed.

#### *Influence of different catalyst on isoamyl acetate yield*

Catalyzing capacity of expandable graphite was compared with some catalysts reported in reference. The results listed in Table 4 illustrated expandable graphite possessed higher catalyzing activity.

**Table 4.** Influence of different catalysts on esterification\*

Catalysts	H <sub>2</sub> SO <sub>4</sub> (96%)	KH <sub>2</sub> PO <sub>4</sub>	Expandable graphite	FeCl <sub>3</sub> ·6H <sub>2</sub> O
Yield of isoamyl acetate, %	92.8	91.2	96.0	72.9

\*KH<sub>2</sub>PO<sub>4</sub> see reference 10, FeCl<sub>3</sub>·6H<sub>2</sub>O see reference 8.

## Conclusions

Through orthogonal experiment, the optimum condition to prepare isoamyl acetate were gained as:  $n(\text{isoamyl alcohol}) : n(\text{acetic acid})=1.5:1$ ,  $w(\text{catalyst with a expandable volume of } 290 \text{ mL}\cdot\text{g}^{-1})=7.5\%$ , reaction time 1.5 h, and temperature keeping at the boiling point. Yield of isoamyl acetate could reach 96.0%.

Expandable graphite possessed higher catalyzing activity in esterification of isoamyl alcohol with acetic acid. The process had the characteristics of smaller mole ratio of isoamyl alcohol to acetic acid, shorter reaction time, and higher yield.

As a kind of polyphase catalyst, expandable graphite could be used in organic reaction which had proton transfer.

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