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Esterification of acetic acid with isoamyl alcohol over expandable graphite catalyst

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ABSTRACT

The catalysis of expandable graphite to esterification of acetic acid with isoamyl alcohol has been studied. X-ray diffraction spectrum of expandable graphite testified the existence of H₂SO₄ intercalation reaction. The influences of catalyst amount, materials ratio, reaction time, expandable volume of the expandable graphite on esterification reaction were studied through L₉(3⁴) orthogonal experiment. Optimum reaction condition were gained as: n(isoamyl alcohol):n(acetic acid)=1.5:1, w(catalyst with a expandable volume of 290mL·g⁻¹)=7.5% total amount of materials, reaction time 1.5h, and temperature keeping at the boiling point. Yield of isoamyl acetate reached 96.0%, and it increased with the expandable volume of expandable graphite. It was testified that expandable graphite was a kind of effective catalyst in the esterification of acetic acid with isoamyl alcohol. © 2008 Trade Science Inc. -INDIA

KEYWORDS

Expandable graphite;
Isoamyl acetate;
Orthogonal experiment;
Catalysis;
Expandable volume.

INTRODUCTION

Expandable graphite is a kind of new material which is prepared through intercalation reaction of H₂SO₄ under the condition of chemical or electric chemistry oxidation^[1,2]. Its application is normally focused on sealing material, adsorbent of oil, after being expanded under high temperature^[3,4]. At the same time, expandable graphite can be used as solid super acid catalyst for its loading to H⁺^[5,6].

Isoamyl acetate is a kind of flavour reagent with fruit taste. It is traditionally prepared with H₂SO₄ as catalyst^[7]. The use of H₂SO₄ often causes the prob-

lems such as corrosion of equipments and pollution of environment. Until now, the tried replacers include FeCl₃, CuSO₄, ferric tri-dodecane sulfonate, FeCl₃/MnO₂, KH₂PO₄, sulfonated polystyrene, TiSiW₁₂O₄₀/TiO₂ and so on^[8-14]. 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. Base on this reason, the catalysis of expandable graphite to esterify reaction between ace-

tic acid and isoamyl alcohol is studied. The influences of catalyst amount, materials ratio, reaction time, expandable volume (EV) of the expandable graphite 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, H_2SO_4 (96%), H_2O_2 (26%), $KMnO_4$, Na_2CO_3 , $CaCl_2$, $NaCl$ were all analytical reagents.

Preparation of expandable graphite

1. Method of C + H_2SO_4 + H_2O_2

Under room temperature, 4.0g of natural graphite was mixed with 10.6mL of 96% H_2SO_4 in a beaker, then a 5.2mL of 26% H_2O_2 was added under stir. After 30 min, products were washed with de-ionized water until pH reached to 6.0~7.0, then dried under 40~60°C and expandable graphite could be gained.

2. Method of C + H_2SO_4 + $KMnO_4$

Under room temperature, 4.0g of natural graphite was mixed with 6.5mL of 96% H_2SO_4 in a beaker, then 0.441g of $KMnO_4$ was added under stir. After 30 min, products were washed with de-ionized water until pH reached to 6.0~7.0, then dried under 40~60°C and expandable graphite could be gained.

3. Method of C + $KMnO_4$ + H_2SO_4 + H_2O_2

Under room temperature, 4.0g of natural graphite was mixed with 7.5mL of 96% H_2SO_4 in a beaker, then 0.441g of $KMnO_4$ was added under stir. After 30min, products were dipped in 10.0mL of 4% H_2O_2 water solution for 15min, and washed with de-ionized water until pH reached to 6.0~7.0, then dried under 40~60°C and expandable graphite could be gained.

Preparation of isoamyl acetate

According to 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 Na_2CO_3 , $CaCl_2$ and $NaCl$, 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

Analyse of expandable graphite

1. X-ray spectrum of natural graphite and 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 0.167nm were two characteristic peaks of natural graphite expanded. Figure 2 was the diffraction spectrum of expandable graphite. Besides the remained character-

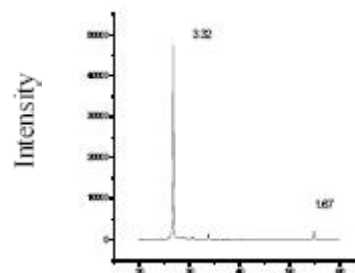


Figure 1: The X-ray diffraction spectrum of natural graphite

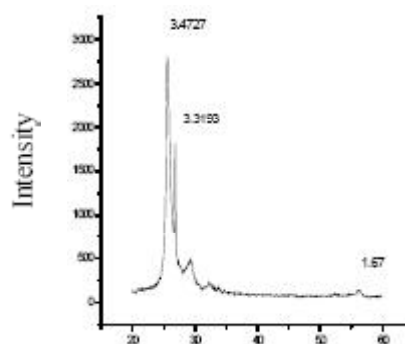


Figure 2: The X-ray diffraction spectrum of expandable graphite

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istic peak 0.332nm of natural expanded, a new diffraction peak of 0.347nm appeared, which testified the change of crystal structure and the existence of intercalation reaction.

2. The EV of expandable graphite

Expandable graphite prepared with different method would contain different dosage of H_2SO_4 , this could be testified by EV of expandable graphite possessed. EV was detected under $900^\circ C^{[15]}$, and the results were listed in TABLE 1. The lager EV expandable graphite possessed, the higher dosage of H_2SO_4 it would hold.

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(isoamyl alcohol):n(acetic acid)=1.5:1, ω (catalyst with a expandable volume of $290 mL \cdot g^{-1}$)=7.5% total amount of materials, reaction time 1.5h, 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(isoamyl alcohol):n(acetic acid)=1.5:1 should be used.

Influence of catalyst dosage on yield

In the range of 2.5%~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 catalyst EV on yield

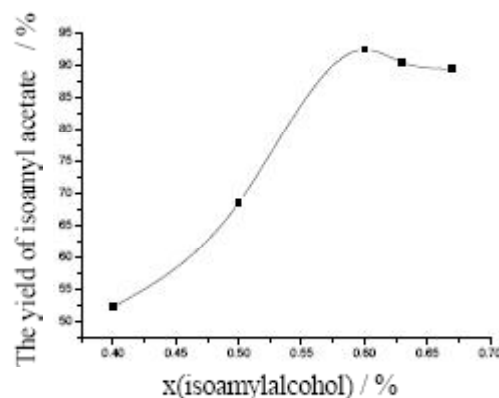
In esterification, expandable graphite could trans-

TABLE 1: EV of expandable graphite prepared with different method

Expandable graphite	C+ $H_2SO_4+H_2O_2$	C+ $H_2SO_4+KMnO_4$	C+ $KMnO_4+H_2SO_4+H_2O_2$
EV $mL \cdot g^{-1}$	180	280	290

TABLE 2 : Results of orthogonal experiment $L_9(3^4)$ for the synthesis of isoamyl acetate

Number	n(isoamyl alcohol): n(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



(Condition: dosage of expandable graphite (EV=290 $mL \cdot g^{-1}$) equal 7.5%, reaction time 1.5h)

Figure 3 : Influence of alcohol/acid mole ratio on esterification conversion

fer proton and accelerate reaction rate. Expandable graphite with different EV should possess different dosage of H_2SO_4 , and then it should have different catalyzing activity. Under the optimum technical condition as mentioned above, the catalyzing capability of expandable graphite prepared with different method 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.

TABLE 3: Influence of EV of expandable graphite on esterification*

EV of expandable graphite mL·g ⁻¹	180	280	290
Yield of isoamyl acetate%	80.0	90.0	96.0

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

TABLE 4 : Influence of different catalyst on esterification*

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

*1. KH₂PO₄ see reference^[10]

Influence of reaction time on yield

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

Selection of dehydrolyzing agent

When the mole ratio of n(isoamyl alcohol) : n(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 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.

2. FeCl₃·6H₂O see reference^[8]

CONCLUSIONS

Through orthogonal experiment, the optimum condition to prepare isoamyl acetate were gained as: n(isoamyl alcohol): n(acetic acid)=1.5:1, w(catalyst with a expandable volume of 290mL·g⁻¹)=7.5%, reaction time 1.5h, 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.

ACKNOWLEDGMENTS

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