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Preparation of expandable graphite loaded with zinc sulfate and its catalytic activity in the synthesis of diisoamyl oxalate

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Abstract: : Expandable graphite loaded with zinc sulfate (EG_{Zn}) was prepared with $KMnO_4$ as oxidant, H_2SO_4 as inserting reagent, $ZnSO_4$ as the auxiliary intercalating agent, and its catalytic activity for esterification between isoamyl alcohol and oxalic acid was studied. Expanded volume and X-ray diffraction were employed to illuminate the intercalating reaction and structure. Influence of mole ratio of isoamyl alcohol to oxalic acid and dosage of EG_{Zn} on ester yield were optimized through single factor experiments. The suitable esterification condition is controlled as follows: molar ratio of isoamyl alcohol to oxalic acid keeps 2.8 : 1.0, mass of EG_{Zn} keeps 7.4% of the total reactants mass, reaction keeps at the boling point and lower than 140°C. Yield of di-isopentyl oxalate reaches 67%. The catalytic activity of EG_{Zn} is stable within the first four time reuse, but it decreases obviously in the fifth time. It was worthy to note that there is no obvious change in EG_{Zn} expansion property.

Key words: Zinc sulfate, Expandable graphite, di-isopentyl oxalate, Catalytic activity, Stability.

Introduction

Di-isopentyl oxalate is a kind of improver for diesel hexadecane number [1], and it can improve the value by 4.0 with only a 1.0 (vol)% additive amount. In addition, di-isopentyl oxalate is constituted by only C, H and O three elements, it can completely burn and reduce the fume, which accords the requirement and development tendency of environmentally friendly production. Oxalic acid is easy oxidized and turned into CO_2 and CO, so concentrated H_2SO_4 can not be used as catalyst of esterification between isoamyl alcohol and oxalic acid. Normally, its preparation is carry out with only isoamyl alcohol, oxalic acid, and a water-carrier agent toluene, which leads to a high mole ratio between alcohol to acid and long reaction period of more than 10 hours.

In recent years, stannic chloride[2], PO_4^{3-}/TiO_2[3], lipase[4] and expandable graphite [5] were reported to use in the synthesis of ester. Zinc sulfate is a kind of Lewis acid, and it has been used as catalyst in the synthesis of n-butyl acetate[6], di-isopentyl oxalate[7] and biodiesel[8]. However, it is soluble in water and hard to separate from reaction system. In order to make it reusable, zinc sulfate should be loaded with suitable carriers.

Expandable graphite (EG) is a kind of composite material, prepared by inserting molecules, atoms or ions into graphite layers, so it was called graphite intercalation compound (GIC). This solid -acid catalyst has exhibited catalysis in the synthesis of ketone [9] and ester [10]. So, the most remarkable thing is that if zinc sulfate is used as auxiliary intercalating agent of graphite, it can not only be loaded in EG, but can also improve the catalytic activity of the GIC. Herein, to obtain expandable graphite loaded with zinc sulfate composite (EG_{Zn}), the intercalation reaction of natural graphite was investigated using $KMnO_4$ as oxidant and $H_2SO_4/ZnSO_4$ as intercalators. In this research, the preparing method of the mentioned EG_{Zn} was founded. Expanded volume and

X-ray diffraction spectroscopy (XRD) were used to characterize the expansiveness and structure, and its' catalytic activity for esterification reaction between isoamyl alcohol and oxalic acid was investigated.

Experimental

WAY refractor (Shanghai, China), Y-4Q X-ray diffractometer (Dandong, China), KSW Muffle furnace, 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. Oxalic acid, isoamyl alcohol, H_2SO_4 (98%), $KMnO_4$, $ZnSO_4 \cdot 7H_2O$, $NaHCO_3$, anhydrous $MgSO_4$ are all analytical reagents.

Preparation of EG_{Zn}

Reactants were weighed and mixed in the order of diluted H_2SO_4, $ZnSO_4 \cdot 7H_2O$, material graphite C and $KMnO_4$ in a 250 mL beaker and stirred at the controlled temperature using a water bath. After maintaining for 40 min, then the solid phase was washed with de-ionized water until pH of the wastewater reached to 6.0−7.0. Solid product was dipped in water for 2 h, then filtrated and dried at 60-65°C for 5 h, and EG_{Zn} was obtained. The effects of various factors on dilatability of the EG_{Zn} were optimized through single factor tests including the dosages of $KMnO_4$, H_2SO_4, $ZnSO_4 \cdot 7H_2O$, H_2SO_4 concentration, reaction temperature and time. Finally, its feasible preparation conditions were determined as follows: mass ratio of C : $KMnO_4$: H_2SO_4(98%) : $ZnSO_4 \cdot 7H_2O$ was controlled as 1.0:0.35:5.0:0.4, and H_2SO_4 was diluted to 80 wt % before reaction; the reaction lasted 40 min at 30°C.

At the same time, EG with only H_2SO_4 as intercalator was prepared under the mass ratio of C:$KMnO_4$:H_2SO_4 (98%) of 1.0:0.35:5.0, H_2SO_4 was diluted to 80 wt %, and the reaction lasted 40 min at 30°C.

Preparation of diisoamyl oxalate

With a definite mole ratio, oxalic acid and isoamyl alcohol were added into the reactor appending stirrer and water segregator. Reaction lasted a certain time at boiling point of less than 140°C and with the catalysis of EG_{Zn}. Then the products were filtrated under vacuum, washed with $NaHCO_3$ saturated solution and deionized water, respectively. The upper layer solution was dried with $MgSO_4$ and then distilled under air pressure, the fraction corresponding to 180 ~210 °C was collected. Then the collected oily distillate was analyzed with refractor and IR, respectively. Refractive index was detected as 1.4204 at 25 °C, similar with the reported value [7]. In the IR spectrum analysis of the distillate shown in Fig 1, characteristic peaks of C-H (2953 cm^{-1}), C=O (1754 cm^{-1}) and C-C-C(=O)-O (1168 cm^{-1}) were all observed except -O-H, which testified the distillate was diisoamyl oxalate. Its yield was calculated according to equation (1).

$$Yield\ \% = (m_{\text{obtained diisoamyl oxalate}} / m_{\text{theory diisoamyl oxalate}}) * 100\% \qquad (1)$$

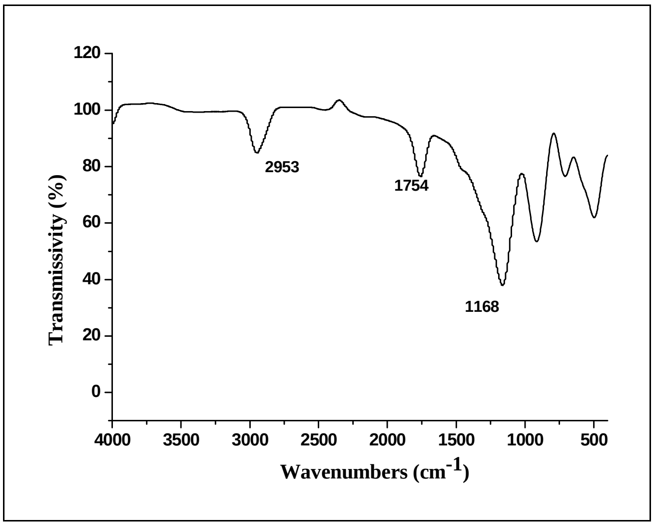

Fig. 1 FTIR analysis of distillate

Results and discussion

Character of EG_{Zn}

Dilatability of EG_{Zn} and EG

Expanded volume (EV) is an important index to judge of the intercalation reaction of H_2SO_4 and $ZnSO_4$ into graphite, and it is defined as the volume of expanded graphite corresponding to 1.0 gram of original GIC, written as mL/g. 0.300 g GIC was weighted and expanded instantly at 930 °C, volume of the obtained expanded graphite was detected with a measuring cup. EV of EG_{Zn} and EG was detected as 500 mL/g and 450 mL/g, respectively. The lager EV expandable graphite possessed, the higher dosage of H_2SO_4 and $ZnSO_4$ it would hold.

X-ray spectrum of the prepared graphite specimens

XRD analysis for natural graphite, EG_{Zn} and expanded graphite, prepared by EG_{Zn} expanded at 930 °C, were performed and shown in Fig. 2. Sharp diffraction peaks at 26.6°, 26.3° and 26.5° appear in natural graphite, EG_{Zn} and expanded graphite, respectively. It is suggested that in the preparation of GIC, the layered structure of the flake graphite is not changed by oxidation and intercalation, but the distance between the layers changes from 0.334 nm to 0.339 nm and 0.336 nm, respectively. Although the structure of the flake graphite is not changed in GIC broadly, the surface structure changed, which wakens the diffraction peak at 55.8°. This can be explained that natural graphite is oxidized under oxidation of $KMnO_4$ and carried on positive charge. Due to the distortion of conjugate system and the exclusive function of positive charge, the gap between graphite layers is extended [11], and then intercalation reaction can be proceed extensively between graphite and intercalating agent. It worthy to note that a new diffraction peaks at 18.9 ° with an interplanar crystal spacing of 0.47 nm can be observed in the diffraction spectrum of EG_{Zn}. At the same time, as observed in Fig. 2 (c), diffraction peaks of 31.7 °, 34.4 °, 36.2 °, 47.5 °, 56.4 °, 62.9 ° and 67.9 ° are characteristic peaks of ZnO, decomposition product of $ZnSO_4$ at high temperature. All the results can testify the intercalation reaction of $ZnSO_4$, and the solid EG_{Zn} product can be used as the catalyst of esterification between oxalic acid and isoamyl alcohol.

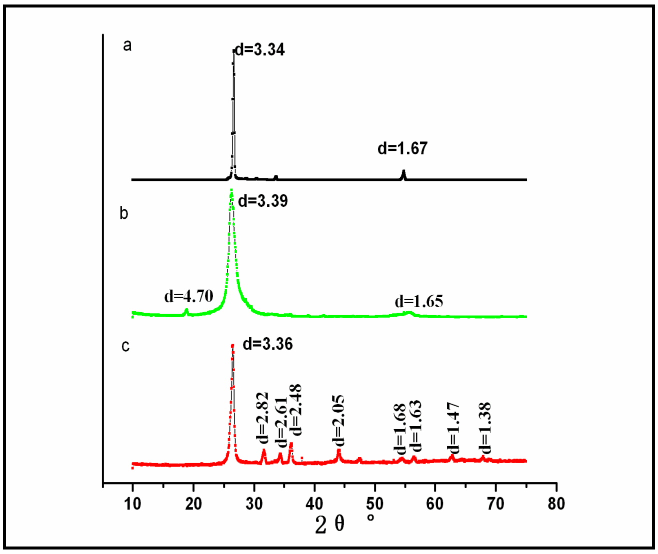

Fig. 2 XRD of natural graphite, EG_{Zn} and expanded graphite
(a) natural graphite; (b) EG_{Zn}; (c) expanded graphite

Optimizing of esterification reaction

Influence of mole ratio between isoamyl alcohol and oxalic acid on ester yield

In esterification, mole ratio of reactants is the most important influence factor on ester yield. Excessive isoamyl alcohol was used in view of its function of acting as water-carrying agent. To find the feasible ratio, isoamyl alcohol to oxalic acid of 2.4 ~ 3.2 : 1.0 was tested with the reaction kept at boiling state, mass of EG set as 7.4% of the total mass of reactants, and reaction stopped until no water separated. As shown in Fig. 3, the reaction gets the highest yield at ratio of 2.8 : 1.0. Ester yield increases with the increase of isoamyl alcohol when the ratio is among 2.4 ~ 2.8: 1.0, beyond this value, it begins to decrease. To high dosage of isoamyl alcohol will increase the wastage of heat, and debase the purity of product. So the mole ratio *n*(isoamyl alcohol) : *n*(oxalic acid) of 2.8: 1.0 is adopted.

Influence of catalyst dosage on yield

With mole ratio of isoamyl alcohol/oxalic acid set as 2.8:1.0, the influence of catalyst dosage on esterification was detected. As tested in single factor experiments, the reaction gets a maximal ester yield of 67% at 7.4 % when the mass of EG_{Zn} is changed in the range of 6.2 % ~ 8.6% of the total reactants mass (shown in Fig. 4). Too high EG_{Zn} dosage will lead to side reaction, and increase loss of product during separation of the catalyst.

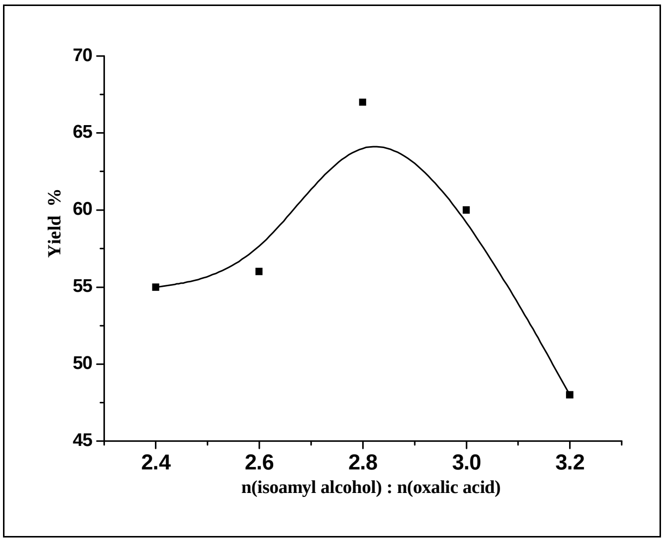

Fig. 3 Influence of isoamyl alcohol/oxalic acid mole ratio on ester yield
(Condition: mass of EG_{Zn} is 7.4 % of the total reactants mass, reaction kept at boiling state until no water separated)

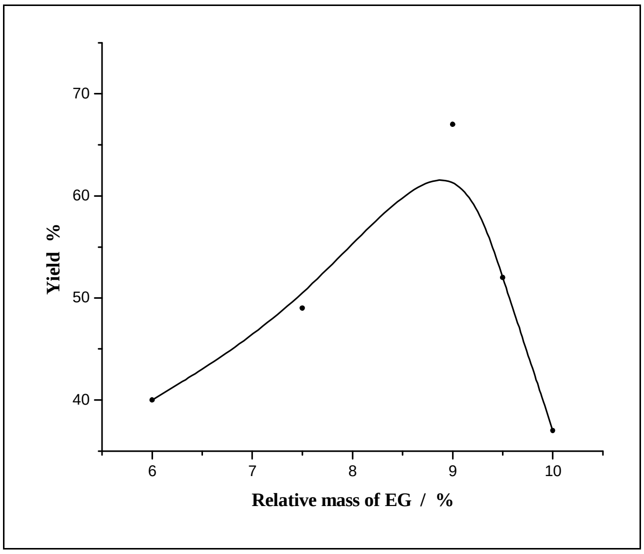

Fig. 4 Influence of EG_{Zn} mass on ester yield
(Condition: ratio of *n*(isoamyl alcohol) : *n*(oxalic acid) controlled as 2.8 : 1.0, reaction kept at boiling state until no water separated)

Comparison of catalytic activity of different catalysts

To investigate difference of catalytic activity of EG_{Zn} and EG, parallel experiments were carried out at the ratio *n*(isoamyl alcohol) : *n*(oxalic acid) of 2.8 : 1.0, reaction kept at boiling state for 1.0h. For EG_{Zn} and EG, 7.4% of total reactants mass was used in the etherification, and the ester yield was 67% and 65%, respectively. The results show that EG_{Zn} presents higher catalytic activity than EG, caused by the auxiliary intercalation and load of $ZnSO_4$.

Influence of water-carrying agent on ester yield

Function of water-carrying agent is to increase the yield of ester through formation of azeotrope with water, which is in favor of the separation of water. Cyclohexane was added with a mass of 2 wt % of total reactants mass, a yield of about 67% obtained, which had no improve in ester yield. The boiling point of azeotrope, composed 8.4% water and 91.6% cyclohexane, is 68.95 °C. Too low temperature decreases reaction rate, and at the same time, the added cyclohexane consumes a large amount of heat energy during distillation and separation of product. When the mole ratio of *n*(isoamyl alcohol) : *n*(oxalic acid) kept as 2.8: 1.0, the superfluous butanol played the role of water-carrying agent. So no additional dehydrolyzing agent is needed.

Feasible condition to prepare diisoamyl oxalate with EG_{Zn} as catalyst

Base on the above experiments, the feasible conditions to get diisoamyl oxalate are described as: *n*(isoamyl alcohol) : *n*(oxalic acid) is controlled as 2.8: 1.0, mass of $\mathbf{EG_{Zn}}$ kept as 7.8 % of total reactants mass, and reaction kept at boiling point until no water separated. Yield of diisoamyl oxalate reach 67%.

Study of recycling rate of EG_{Zn}

The recycling experiment of EG_{Zn} indicates that this catalyst possesses high stability. After reused for four times, the ester yield still can reach 63%. But it suddenly decreases to 10% used in the fifth time. The result is caused by the change of EG_{Zn} edge structure and increasing the mass transfer resistance between solid-liquor phases, which leads to a lower catalytic activity in a limited time. It is worthy to note that the expanded volume of EG_{Zn} has no obvious change, still keeps as 500 mL/g. So esterification reaction can not change the expanding capacity of EG_{Zn}, it can be used as sealing and adsorbing material subsequently.

Conclusions

EG_{Zn} can be prepared according to the mass ratio C:$KMnO_4$:H_2SO_4(98%): Zn SO_4 of 1:0.35:5.0:0.4, H_2SO_4 is diluted to 80 wt %, and intercalating reaction lasts 40 min at 30°C. Its expanded volume is 500 mL/g when expanded at 930 °C. EG_{Zn} shows catalysis activity for esterification of isoamyl alcohol and oxalic acid, and the feasible conditions should be controlled as: *n*(isoamyl alcohol):*n*(oxalic acid) kept 2.8:1.0, weight of EG_{Zn} controlled as 7.4 wt % of total reactants mass, and reaction kept at boiling point. Yield of diisoamyl oxalate is 67%. As a catalyst of esterification, EG_{Zn} presents high stability, easy decentralization and separation in and after the reaction, and it needs smaller mole ratio of isoamyl alcohol to oxalic acid and shorter reaction time.

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