THE CATALYTIC SYNTHESIS OF ETHYL BENZOATE WITH EXPANDABLE GRAPHITE AS CATALYST UNDER THE CONDITION OF MICROWAVE HEATING

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ABSTRACT
Graphite is a kind of crystal compound with layer structure and its intercalating compound named expandable graphite (EG) can be prepared when non-carbonaceous reactants are inserted into graphite layers through chemical or electrochemical reaction. In this research, a kind of EG preprocessed with sulfuric acid was prepared and its catalytic activity in synthesis of ethyl benzoate was tested under the condition of microwave heating. The influence of reaction temperature, microwave power, mole ratio of benzoic acid to ethanol, dose of EG and cyclohexane on ethyl benzoate yield was investigated through single-factor experiment. X-ray and FTIR results confirm the intercalating reaction in graphite. The optimization results of ethyl benzoate synthesis experiment are: the mole ratio of benzoic acid to ethanol is 1.0:5.0, EG is loaded with a weight ratio of 8% of the total benzoic acid and ethanol mass, keeps the reaction at 85°C under a microwave radiation power of 135 W and dose of cyclohexane is 15 mL. Under this condition, the ethyl benzoate yield can reach 80.1% within about 1.5 h, and the catalytic activity of EG shows no significant decrease in the 3rd time reutilization. However, it’s obviously decreased in the 4th time. Nevertheless, the EG expanded volume has no obvious change. Microwave heating is an effective method in the synthesis of ethyl benzoate.

Keywords: Ethyl benzoate, Expandable graphite, Microwave heating, Catalytic activity, Cyclohexane, Reutilization

INTRODUCTION
Ethyl benzoate is a kind of organic ester mainly existed in fruits such as peach, grape, cherry, pineapple. It has been widely used as solvent of cellulose, resin, and it’s also available for the preparation of Ylang Ylang oil, essence of soap, tobacco, berries and so on due to its low toxicity. In consideration of ethyl benzoate’s wide application in chemistry industry, daily supply and food manufacture, its production is of great importance.

As for the chemical synthesis of ethyl benzoate, H₂SO₄ may be the first used catalyst due to its high catalytic activity. Whereas, this kind of catalyst is difficult to reclaim and with serious corrosive effect for equipment, dehydration and carbonification effect for organic reactants and products. Stannic chloride (Ma and Li, 2004), PO₄³⁻/TiO₂ (Zhang et al., 2011), lipase (Ghamgui et al., 2006), ZnSO₄ (Liao et al., 2004), ZnO (Qian et al., 2011) and so on had been reported in the synthesis of ester. Although the preparation of Yb(N(SO₂CF₃)₂)₃ was very complex (Wang et al., 2003), it presented high catalytic activity in the esterification of ethanol and benzoic acid, and the ethyl benzoate yield was over 99% under the optimum conditions of catalyst mass ratio of 8%, molar ratio of ethanol to benzoic acid of 7:1, reflux time of 6 h.

While, the chitosan sulfate powder prepared with chemical precipitation method improved the yield to 86.5% within 3.0 h (Liu and Wang, 2003). Expandable graphite (EG) is a kind of graphite intercalation compound normally preprocessed with sulfuric acid (Shioyam and Fujii, 1987), and the formation of the graphite sulfate as showed in equation (1) (Liu and Song, 1998) makes it turn into a solid acid catalyst. Therefore, EG has exhibited catalysis in the synthesis of ketones (Zhang et al., 2007) and esters (Pang, 2014). Furthermore, EG can be prepared with cheap material under gentle reaction temperature, and it’s also easy to disperse, recycle when used in reaction.
n\left( {\text{graphite}} \right) + n{H_2}S{O_4} + \frac{n}{2}\left[ {O} \right] \to \left[ {\text{graphite}} \cdot HSO_4^ - \right]_n \cdot H_2SO_4 + \frac{n}{2}\ HO \quad \left( 1 \right)

\begin{align*}
\text{[O]} & : \text{oxidant; [graphite} \cdot \text{HSO}_4^- \cdot \text{H}_2\text{SO}_4]: \text{the produced graphite sulfate} \\
\text{Microwave heating is becoming a widely accepted tool for synthetic chemists since 1986 (Gedye \textit{et al.}, 1986). It’s possible to improve product yield, enhance reaction rate, and it’s also a safe and convenient method for reaction system heating (Kerep and Ritter, 2006; Kristen and Nicholas, 2007). The catalytic mechanism of microwave heating is that the energy level of the microwave is exactly matched with the rotational energy level of the polar molecule. When it’s absorbed by polar molecules, the reaction activity will be greatly improved. Therefore, microwave heating has been successfully used in the field of chemical synthesis (Puciova \textit{et al.}, 1994; Li and Yin, 2002). However, there is no report on its application to the synthesis of ethyl benzoate with EG as catalyst. Therefore, in this research, EG was prepared with KMnO_4 as oxidant and H_2SO_4 as inserting reagent; and its catalyst for esterification of benzoic acid and ethanol was studied under the microwave heating condition. The influence of reaction temperature and microwave power, mole ratio of benzoic acid to ethanol, dose of EG catalyst and cyclohexane water-carrying reagent on ethyl benzoate yield was tested. Catalytic activity differences between the EG and H_2SO_4, and differences between the EGs with different repetition times were investigated.

\textit{MATERIALS AND METHODS} \\
A 650 full-automatic refractometer (Shandong, China), XH-300ULY-4Q microwave ultrasonic UV synthesizer (Beijing, China), X-ray diffractometer (XRD) (Dandong, China), KSW Muffle furnace (Tianjin, China), FTS-40 Fourier transform infra-red (FTIR) spectrometer (America Biorad) were used in this experiment.

Natural flake graphite with an average diameter of 0.30 mm and a carbon content of 96% was provided by Qingdao Xite Carbon Co. Ltd., China. Ethanol, benzoic acid, cyclohexane, H_2SO_4 (98%), KMnO_4, NaHCO_3, anhydrous Na_2CO_3 were all analytical reagents.

\textit{Preparation and Characterization of the EG Catalyst} \\
Reactants were weighed as per the mass ratio C:75%H_2SO_4:KMnO_4 of 1.0:6.67:0.15 (Pang and Liu, 2010) and mixed in the order of diluted H_2SO_4, natural graphite C and KMnO_4 in a 250 mL beaker. The intercalation reaction totally lasted 30 min at 30°C controlled with a water bath. 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 then EG catalyst obtained. The expanded volume of the EG at 800°C is detected as 520 mL/g.

XRD data of the prepared EG were recorded under the operation condition of 40 kV, 30 mA, employing Cu Kα radiation with a Ni filter (wavelength \(\lambda=0.15418\) nm) at a scan rate of 0.06°/S and 2θ ranging from 15° to 70°. The interlayer spacing was obtained as per Bragg’s law. As showed in Figure 1, EG presents the same characteristic diffraction peaks like natural graphite at about 26° and 55°, which indicates EG still keeps the layer structures. Whereas, the (002) diffraction peak transfers to a smaller angle of 25.9°, and corresponds to a big interplanar crystal spacing of 3.44 Å at the same time. This can be explained that natural graphite is oxidized by KMnO_4 and then it presents positive charges. Then gap between graphite layers is extended due to the repulsion, and intercalation reaction can proceed between graphite and intercalators. The positive charges of the oxidized graphite network are balanced by negatively charged acid anions and also including molecules, and then the graphite sulfates come into being as showed in equation (1).

The FTIR spectra of the prepared EG was recorded between 4000~400 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). Sample was prepared by the mixture of EG powder and KBr at a mass ratio of about 1:100. As can be seen from Figure 2, the prepared EG shows the characteristic stretching vibration absorption peaks of -OH (round 3400 cm\(^{-1}\)), caused by the intercalation of H_2SO_4/HSO_4\(^{-}\) (Shioyam and Fujii, 1987). In the range of 2930~2850 cm\(^{-1}\), the symmetry and dissymmetry stretching vibration absorption of CH_2 are observed, which should be the results of a part of C=CH being damaged. The peaks at about 1630 cm\(^{-1}\) are the specific absorption of the C=C stretching vibrations, originating from the graphite conjugated
structure. The strong stretching vibration absorption peaks of sulphate are also observed round 1120 cm\(^{-1}\).

**Figure 1:** XRD Spectra of Graphite and the EG  
**Figure 2:** FTIR Spectrum of the EG

**Preparation and Characterization of Ethyl Benzoate**

With a definite mole ratio, benzoic acid, ethanol, water-carrying reagent and catalyst were added into the three-necked bottle appended with thermometer, magnetic stirrer, water segregator and reflux condenser. Reaction occurred under a setting microwave heating power and temperature until no water divided from the reactor. When it was cooled to room temperature, the products were filtrated under vacuum, washed with NaHCO\(_3\) saturated solution and deionized water respectively. The upper layer solution was dried with Na\(_2\)CO\(_3\) and then distilled under air pressure, the fraction corresponding to 208~213°C was collected. Then, the collected oily distillate was analyzed with refractor and IR respectively.

Refractive index of the collected oily distillate is detected as \(n_d^{20}=1.5001\), and it’s similar with the reported value of ethyl benzoate of 1.5007.

**Figure 3:** (a) FTIR of the Ethyl Benzoate and (b) the Collected Distillate
The FTIR spectrum of the distillate was detected and showed in Figure 3. Except the -O-H, the characteristic peaks of C-H in aromatic ring (3067 cm⁻¹), C-H in methyl (2984cm⁻¹), and acyl C=O (1720 cm⁻¹), C=C (1599cm⁻¹, 1454 cm⁻¹), C-O (1275 cm⁻¹, 1109cm⁻¹) are all observed. The result is similar with the standard spectrum of ethyl benzoate, and therefore, the collected distillate is ethyl benzoate. In all the tested experiments, ethyl benzoate yield was calculated according to equation (2).

\[
\text{Yield} = \frac{\text{obtained ethyl benzoate}}{\text{theory ethyl benzoate}} \times 100\%
\]

RESULTS AND DISCUSSION

Influence of Reaction Temperature on Ester Yield

According to the preliminary experiment, reaction temperature was found to be the most important factor. So, with the microwave heating power setting as 135 W, mole ratio of benzonic acid to ethanol as 1:5, dose of cyclohexane as 10 mL and EG as 8 wt% of the total benzonic acid and ethanol mass respectively, the influence of reaction temperature on ethyl benzoate yield was tested with the synthesizer setting as temperature controlled style. As showed in Table 1, there is no product obtained when the temperature is lower than the water-cyclohexane azeotropy temperature of 69°C. Whereas, when it's above 69°C, ethyl benzoate yield increases with the temperature going up and then reaches a stable level of 55.1%. Too high temperature will cause the excessive gasification of ethanol and its decrease in liquid reaction system. Therefore, the reaction temperature can be controlled as 85°C.

<table>
<thead>
<tr>
<th>Temperature /°C</th>
<th>60</th>
<th>65</th>
<th>70</th>
<th>75</th>
<th>80</th>
<th>85</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Benzoate Yield /%</td>
<td>0</td>
<td>0</td>
<td>19.7</td>
<td>34.4</td>
<td>54.2</td>
<td>55.3</td>
<td>55.1</td>
</tr>
</tbody>
</table>

Influence of Mole Ratio of Benzonic Acid to Ethanol on Ester Yield

To find the feasible mole ratio of benzoninic acid to ethanol, a series of experiments were carried out with the reaction temperature setting as 85°C (corresponding to the heating power of 135 W), dose of cyclohexane as 10 mL and EG as 8 wt% of the total benzonic acid and ethanol mass respectively. As showed in Table 2, the yield increases with the acid to ethanol mole ratio increasing in the range of 1:1~1:7, and then it begins to decrease. To high dosage of ethanol will debase the relative concentration of acid. So, the mole ratio of 1:5 is adopted.

<table>
<thead>
<tr>
<th>Benzonic Acid to Ethanol Mole Ratio</th>
<th>1:1</th>
<th>1:3</th>
<th>1:4</th>
<th>1:5</th>
<th>1:6</th>
<th>1:7</th>
<th>1:10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Benzoate Yield /%</td>
<td>32.5</td>
<td>53.6</td>
<td>67.1</td>
<td>69.4</td>
<td>69.9</td>
<td>70.1</td>
<td>69.3</td>
</tr>
</tbody>
</table>

Influence of EG Dosage on Ester Yield

With the reaction temperature setting as 85°C (corresponding to the microwave heating power of 135 W), mole ratio of benzonic acid to ethanol as 1:5 and dose of cyclohexane as 10 mL, the influence of catalyst dose on yield was detected. As tested in single factor experiments, ethyl benzoate yield increases with the EG dose increasing in the range of 0~15 wt%. But the improvement becomes slow when the dose is above 8 wt% as showed in Table 3. Therefore, the relative weight of EG can be set as 8 wt% of the total benzonic acid and ethanol mass.

<table>
<thead>
<tr>
<th>Dose of EG /%</th>
<th>0</th>
<th>5</th>
<th>8</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Benzoate Yield /%</td>
<td>0</td>
<td>60.5</td>
<td>69.8</td>
<td>70.0</td>
<td>71.3</td>
</tr>
</tbody>
</table>
Influence of Cyclohexane Dose on Ester Yield
Function of water-carrying reagent is to increase the yield of ester through formation of azeotrope holding a lower boiling point, which is in favor of the separation of water under a low temperature. When cyclohexane is tested, boiling point of cyclohexane-water azeotrope is 68.95 °C. With the reaction temperature setting as 85°C (corresponding to the microwave heating power of 135 W), mole ratio of benzonie acid to ethanol as 1:5, and the relative wt% of EG as 8%, the influence of cyclohexane dose was tested in the range of 0~20 mL. As showed in Table 4, ethyl benzoate yield increases with the cyclohexane volume increasing. But the improvement becomes slow when the dose is above 15mL. So, the 15 mL cyclohexane can carry out the produced water.

<table>
<thead>
<tr>
<th>Dose of Cyclohexane /mL</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Benzoate Yield %</td>
<td>64.8</td>
<td>70.5</td>
<td>76.2</td>
<td>76.0</td>
<td></td>
</tr>
</tbody>
</table>

Influence of Microwave Heating Power on Ester Yield
Microwave heating is becoming a widely accepted tool for organic synthetic reaction. With the reaction temperature setting as 85°C, mole ratio of benzonie acid to ethanol as 1:5, the relative wt% of EG as 8% and volume of cyclohexane as 15 mL, the influence of microwave heating power was tested in the range of 110~140 W under a power controlled style. The results listed in Table 5 show that the microwave power has important influence on the ethyl benzoate yield. The ethyl benzoate yield, at first, increases with the heating power increasing, and when it rises to the level of 135 W (corresponding to 85°C), the ethyl benzoate yield reaches 80.1%. While, too high power will cause high reaction temperature and by-reactions.

At the same time, contrast tests between normal heating with electric heater and microwave heating (corresponding to the power of 135 W) were carried out under the condition of reaction temperature as 85°C, mole ratio of benzonie acid to ethanol as 1:5, dose of EG as 8 wt%, volume of cyclohexane as 15 mL. The conventional heating method has only one heat source, the heating starts from the object surface, and then it gradually transfers by heat conduction and heat convection inside the deep body. Therefore, the heating speed is very slow and the esterification only gets a low ethyl benzoate yield of 68.1% within about 1.5 h. As for the microwave style, the reaction temperature is uniform in the total reaction system due to the strong penetrating ability of the microwave. So, it can shorten the reaction time and show high effectivity and yield than the ordinary heating method (Liu and Wang, 2003; Wang et al., 2003).

<table>
<thead>
<tr>
<th>Microwave Power / W</th>
<th>110</th>
<th>115</th>
<th>120</th>
<th>125</th>
<th>130</th>
<th>135</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Benzoate Yield /%</td>
<td>69.7</td>
<td>70.2</td>
<td>74.3</td>
<td>76.2</td>
<td>77.1</td>
<td>80.1</td>
<td>78.8</td>
</tr>
</tbody>
</table>

Feasible Condition of Ethyl Benzoate Preparation with EG as Catalyst under the Condition of Microwave Heating
According to the above mentioned experiments, with EG as catalyst, the feasible conditions to get ethyl benzoate under microwave heating style are described as follows: mole ratio between benzonie acid and ethanol equals 1:5, the dose of EG is 8 wt%, volume of cyclohexane keeps 15 mL, the reaction temperature is controlled at 85°C with a microwave heating power of 135 W. The ethyl benzoate yield can reach 80.1% within about 1.5 h, and the reaction is easy to control.

Comparison of Catalytic Activity
To investigate catalytic activity difference between the EG and the traditional H₂SO₄ with a weight concentration of 98%, and difference between the EGs with different repetition times, parallel and contrasted experiments were carried out under the mentioned reaction conditions. Results listed in Table 6 show that EG presents higher catalytic activity than H₂SO₄, which is due to the former can effective control the dehydration and carbonification effect for organic reactants and products. The recycling
experiments of the EG indicate that this catalyst possesses high stability. After reused for three times, the ester yield can still reach 72.4%. But it suddenly decreases to 30.8% when the EG repeated in the 4th time. The results should be caused by the change of EG edge structure, which increases the mass transfer resistance between solid-liquor phases and leads to a lower catalytic activity in a limited time. It is worthy to note that the detected expanded volume of EG has no obvious change; it still maintains at 510 mL/g. So, esterification reactions cannot change expandable capacity of the EG.

| Table 6: The Catalytic Activity Difference between Different Catalysts |
|------------------|-----------------|-----------------|-----------------|-----------------|
| Catalysts        | H2SO4(98%)      | EG for the 1st Time | EG for the 2nd Time | EG for the 3rd Time | EG for the 4th Time |
| Ethyl Benzoate Yield | %              | %               | %               | %               |
| Ethyl Benzoate Yield | 63.8           | 80.1            | 78.1            | 72.4            | 30.8            |

**Conclusion**

The EG prepared with KMnO4 as oxidant and H2SO4 as intercalator shows well catalytic activity in esterification of ethanol and benzoic acid under the following conditions: mole ratio of benzoic acid to ethanol is 1:5, reaction keeps 85°C with a microwave heating power of 135W, dose of cyclohexane and the EG is 15 mL and 8 wt% respectively. Ethyl benzoate yield can reach 80.1%. The EG presents high stability and it’s easy decentralization and separation; the reaction needs smaller ethanol to benzoic acid mole ratio and shorter reaction time than H2SO4 and others. Microwave heating is an effective method in esterification of ethanol and benzoic acid.

**ACKNOWLEDGEMENTS**

The authors would like to thank Natural Science Foundation of Hebei Province (CN) (No. B2015201028) for financial support.

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