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Synthesis of ethyl p-hydroxybenzoate catalyzed by $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}]\cdot 8\text{H}_2\text{O}$ with Waugh structure

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ABSTRACT

$(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}]\cdot 8\text{H}_2\text{O}$ with Waugh structure was used as a catalyst for synthesizing ethyl p-hydroxybenzoate. Control variate method was adopted to determine reaction conditions. Optimum conditions determined by experiment: alcohol acid mole ratio was 4:1; 0.2g catalyst and 3ml water-carrying reagent were used; reaction time was 2.0h; 2 conversion rate reached 96.3%.

Key words: Waugh structure, Catalyst, ethyl p-hydroxybenzoate

INTRODUCTION

Para-hydroxybenzoic acid ester, also called nipagin ester, usually refers to the ester produced by para-hydroxybenzoic acid reacted with C1 ~ C7 alcohol. Owing to its high performance, broad spectrum, high compatibility, and wide pH scope, nipagin ester is widely used in many fields including organic synthesis, foods, cosmetics, medicine, potables, feedstuff, and film. Traditionally, concentrated sulfuric acid is usually used as the catalyst for synthesizing nipagin ester. This method can cause serious equipment corrosion, too many by-products, complexity in product segregation, and pollution of the environment, so it can't adapt to the new production requirements any more. Researchers at home and abroad have developed many other catalysts like solid acid, solid heteropoly acid, vitamin C, and ionic liquid, which have better effect. In recent years, most relevant studies concern Keggin, Dawson and Anderson structure polyoxometalate anions, leaving catalyst studies on Waugh structure polyoxometalate anions at an early stage [1-5].

MATERIALS AND METHODS

1.1 Instrument and Reagents

T32 Semi Micro Organic Preparation Instrument (Tianjin Glass Instrument Factory), Nicolet is5 Fu Liye infrared analyzer(Themofisher Scientific Co., Ltd.)

P-hydroxybenzoic acid, absolute ethyl alcohol, sodium carbonate solid, benzene, methylbenzene, cyclohexane etc (analytically pure).

1.2 Test method

1.2.1 Catalyst Preparation

A certain amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was weighed out and dissolved in quantitative water, adjusted with glacial acetic acid to pH 4-6 and heated until boiling; then a certain amount of $\text{MnSO}_4\cdot \text{H}_2\text{O}$ was dissolved in hot water, mixed with the solution above, agitated and heated until boiling, where there was yellow precipitate; a certain amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution was added thereto, heated until orange-red solution, disposed at room temperature for hours, after which there was orange red crystal. Vacuum filtration and recrystallization was performed three

times followed by drying at 70-80 °C to obtain orange red crystal, which was found to be rhombus under 5×40 microscope[6].

1.2.2 Synthesis of ethyl 4-hydroxybenzoate

First of all, precisely take a certain volume of alcohol, as well as a certain amount of solid para-hydroxybenzoic acid and $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 8\text{H}_2\text{O}$ catalyst of Waugh structure, then take several zeolite, and put them to a 50mL three-necked flask in turn. Add an appropriate amount of distilled water to the water separator, add a certain amount of methylbenzene as the water-carrying agent to the constant pressure dropping funnel; boil it, and then drop the methylbenzene to the three-necked bottle drop by drop. After the reaction ends, filter out the catalyst when it's still hot. Distil the unreacted alcohol off and recover it, and then calculate the esterification rate of the product.

Use an appropriate amount of distilled water, Na_2CO_3 solution with 5% mass fraction, and an appropriate amount of distilled water to wash the crystal produced after the reaction in turn, and then use a suction filtration pump for suction filtration and then air-dry it to get the raw ester. Heat the raw ester using the absolute ethyl alcohol, distilled water, and active carbon at a certain ratio and then recirculate it for some time to get the pure ester. Determine the melting point of the crystal and make infrared spectrum analysis[7-8].

1.2.3 Selection of water-carrying reagent

As this catalyst is easily decomposed when heated under weak current and aqueous condition, thus in order to protect catalyst, water must be removed from reaction system, in which case, water-carrying reagent is commonly added. In this experiment, methylbenzene, cyclohexane and benzene served as water-carrying reagents for researching its effect on esterification rate. In this experiment, alcohol acid mole ratio was 4:1, 0.3g catalyst and 3mL water-carrying reagent were used and reaction time was 1.5h; experimental result was shown below:

Table 1 Optimum Different Water-Carrying Reagents Determination

Water-Carrying Agents	Cyclohexane	Methylbenzen	Benzene
Esterification Rate%	65.5	79.3	62.7

As shown in Table 1, the same amount of methylbenzene had high water-carrying capacity under the same reaction conditions, thus methylbenzene was chosen as water-carrying reagent.

1.2.4 Water-Carrying Agent Amount Selection

For protection of catalyst, water shall be separated from reaction system, entailing methylbenzene as water-carrying agent. Alcohol-acid molar ratio was consistently 4:1, catalyst amount 0.3 g, reaction time 1.5h, only with water-carrying agent amount changed. The rates are shown in Table 4:

Table 2 Optimum Water-Carrying Agent Amount Determination

Water-Carrying Agent Amount(mL)	1.0	2.0	3.0	4.0
Esterification Rate%	72.8	81.3	89.9	77.1

As shown in Table 2, when methylbenzene use level reached 3mL, maximum esterification rate was achieved; when use level was excessively high or low, yield was relatively low possibly because esterification reaction was one reversible reaction, addition of water-carrying reagent at the beginning can carry away water generated in reaction, but addition of excessive water-carrying reagent not only decreased alcohol and acid concentrations but also reduced temperature of reaction system, thus 3mL was chosen as water-carrying reagent use level.

1.2.5 Optimum Selection of Alcohol-Acid Molar Ratio

Catalyst amount was consistently 0.3 g, methylbenzene 3 mL, reaction time 1.5h, with alcohol-acid molar ratio changed. The rates are shown in Table 3:

Table 3 Optimum Alcohol-Acid Ratio Determination

Alcohol-Acid Molar Ratio	2:1	3:1	4:1	5:1	6:1
Esterification Rate%	64.4	73.3	79.3	78.1	74.9

Table 3 shows that, as the molar ratio of alcohol acid increases gradually, the esterification rate of ethyl p-hydroxybenzoate will rise first and then decline. When the molar ratio of alcohol acid increases to 4:1, the esterification rate is the highest, so the molar ratio of alcohol acid shall choose 4:1.

1.2.6 Catalyst Amount Selection

Alcohol-acid molar ratio was consistently 4:1, water-carrier agent 3 mL, reaction time 1.5h, only with catalyst amount changed. The rates are shown in Table 4:

Table 4 Optimum Catalyst Amount Determination

Catalyst Amount (g)	0.1	0.2	0.3
Esterification Rate (%)	83.5	85.7	79.3

As shown in Table 4, when catalyst use 0.2g, maximum esterification rate was achieved, thus 0.2g was chosen as catalyst use level.

1.2.7 Reaction Time Selection

Alcohol-acid molar ratio was consistently 4:1, catalyst amount 0.2 g, water-carrier agent 3 mL, only with reaction time changed. The rates are shown in Table 5:

Table 5 Reaction Time Determination

Reaction Time (h)	1	1.5	2	2.5
Esterification Rate (%)	72.8	89.9	96.3	96.1

Table 5 shows that the esterification rate increases as the reaction time increases; when the reaction time is 2h, the esterification rate reaches the biggest value, and when time expands, the esterification rate maintains basically unchanged. In order to save time, the reaction time shall be 2h.

1.2.8 Parallel Experiments on Optimum Condition

Reaction time was consistently 2h, alcohol-acid molar ratio 4:1, catalyst amount 0.2g, water-carrying agent amount 3mL. The rates are shown in Table 6:

Table 6 Parallel Experiments on Optimum Condition

Parallel Experiments	1	2	3	4
Esterification Rate (%)	96.3	95.9	96.1	95.8

Table 6 shows that when $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 8\text{H}_2\text{O}$ of Waugh structure is used as the catalyst to synthesize ethyl p-hydroxybenzoate, it can ensure the best conditions in repeated tests, and the results of the four repeated tests are basically the same.

1.2.9 Catalyst Reusability

Filter out the catalyst when it's still hot, and wash and dry it and then use it for follow-up reaction directly. Observe the performance of the catalyst for repeated use under the best condition, and the test result is shown in table 7 below.

Table 7 Catalyst Reusability

Catalyst Reuses	1	2	3	4
Esterification Rate (%)	96.3	93.2	89.7	78.4

As shown in Table 7, catalytic activity of catalyst gradually decreased with increasing number of uses, but after catalyst was used for four times, esterification rate was still as high as 78.4%, suggesting that this catalyst enjoyed relatively high stability and can be reused for many times under such conditions.

1.3 Product analysis and determination of physical constants

Refined ethyl p-hydroxybenzoate is white powdered form crystal; its melting point is 115 - 117°C, which is basically the same as that mentioned in the literature. Infrared analysis of ethyl p-hydroxybenzoate shows that at 3202cm^{-1} , there is O—H stretching vibration of phenol, at 1684cm^{-1} , there is C = O double-bond stretching vibration, and at 1447cm^{-1} , there is an absorption peak of benzene skeleton vibration. At 1291cm^{-1} and 1245cm^{-1} , there are absorption peaks of stretching vibration of aromatic ester; at 1170cm^{-1} , there is an absorption peak of stretching vibration of C-OH. At $3000\text{cm}^{-1} \sim 2750\text{cm}^{-1}$, there are two absorption peaks of stretching vibration, that's the absorption peak of stretching vibration of $-\text{CH}_2-\text{CH}_3$. This agrees with the standard IR spectrogram of ethyl p-hydroxybenzoate, which shows that the synthetic product is ethyl p-hydroxybenzoate [9].

CONCLUSION

Research showed that $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 8\text{H}_2\text{O}$ with Waugh structure was one excellent catalyst for preparing ethyl p-hydroxybenzoate ; optimum process conditions for synthesizing ethyl p-hydroxybenzoate : alcoho-lacid mole ratio was 4:1; 0.2g catalyst and 3mL water-carrying reagent methylbenzene were used; reaction time was 2h; ethyl p-hydroxybenzoate yield can reach 96.3%.

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