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Synthesis of Butyl Acetate Catalyzed by $(NH_4)_6[MnMo_9O_{32}]8H_2O$ with Waugh structure

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ABSTRACT

Synthesis conditions of butyl acetate were studied with catalysis by Waugh structure molybdenum-manganese polyoxometalate. Optimum reaction condition was determined as the following: alcohol-acid molar ratio 1:3, catalyst quantity 0.4 g, methylbenzene 5 ml as water-carrying agent, reaction time 120 min, selectivity 100%, esterification rate 93.50%.

Keywords: Waugh Structure Molybdenum-Manganese Polyoxometalate Catalyst Butyl Acetate

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INTROUDUCTION

Butyl acetate is a colorless, transparent liquid with pleasant fruit-like scent that is approved by China for natural equivalent edible flavor. It also serves as an indispensable organic chemical raw material, used widely across solvents, paints and medical industries [1]. In butyl acetate synthesis process, concentrated sulfuric acid is traditionally used as catalyst, with glacial acetic acid and n-butyl alcohol reacting directly with each other in esterification. It is a cost-efficient, highly active method, however, with serious corrosion of instrument, large discharge of waste acid and therefore serious air pollution. As the international environmental laws and regulations become increasingly strict, it is advisable trend to find a green catalyst with low catalytic amount, reasonable price, environment-friendliness, easy recycling, reusability. Heteropoly acid is an extremely strong Bronsted acid, which, as an acidic catalyst, is characterized by low usage amount, no pollution, no corrosion of instrument and reusability when compared to conventional mineral acid. In recent years, most relevant studies [2-5] concern Keg gin, Dawson and Anderson structure polyoxometalate anions, leaving catalyst studies on Waugh structure polyoxometalate anions at an early stage.

MATERIALS AND METHODS

1.1 Instrument and Reagents

T32 Semi Micro Organic Preparation Instrument (Tianjin Glass Instrument Factory), GC122 Gas Chromatograph (Shanghai Precision & Scientific Instrument Co., Ltd.), WTA-2W Abbe Refractometer (Shanghai Precision & Scientific Instrument Co., Ltd.), FTIR-8400S Fourier Transform Infrared Spectrometer (Shimadzu Co., Ltd., Japan).
Glacial acetic acid, butyl alcohol, solid sodium chloride, solid sodium carbonate, anhydrous magnesium sulfate, anhydrous calcium chloride, cyclohexane, methylbenzene, etc., all of which were AR.

1.2 Methods

1.2.1 Catalyst Preparation

A certain amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 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 $MnSO_4\cdot H_2O$ was dissolved in hot water, mixed with the solution above, agitated and heated until boiling, where there was yellow precipitate; a certain amount of $(NH_4)_2S_2O_8$ 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℃ to obtain orange red crystal, which was found to be rhombus under 5×40 microscope[6-8].

1.2.2 Butyl Acetate Synthesis

The reaction was performed in a reaction instrument consisting of three-necked flask, water knockout drum, reflux condensing tube, constant pressure funnel, and thermowell, which was heated by electric jacket. A certain amount of catalyst, zeolite, glacial acetic acid, butyl alcohol was added to the three-necked flask. 3.5 mL of high purity water was added to water knockout drum. A certain amount of water-carrying agent was added to separating funnel. After a period of heating and reflux, the liquid was poured out, and the solid catalyst was recycled; the liquid was left at rest for separation, where the oily part was washed with saturated sodium carbonate solution to neutral, then with saturated sodium chloride 2-3 times, then with saturated calcium chloride 2-3 times, and finally dried with anhydrous magnesium sulfate, and left at rest. The solution was poured out and distilled to collect 124-126 ℃ cut fraction, where lied butyl acetate[9-10].

1.2.3 Esterification Rate Determination

The residual amount of acetic acid was determined by titration of a certain amount of mixture with standard NaOH solution, and the esterification rate of acetic acid was determined by the following formula:

Esterification Rate = (Initial amount of substance of acetic acid – final amount of substance of acetic acid) / Initial amount of substance of acetic acid × 100%

2. Experiment Results

2.1 Optimum Selection of Alcohol-Acid Molar Ratio

Catalyst amount was consistently 0.4 g, water-carrier agent 3 mL, reaction time 60 min, with alcohol-acid molar ratio changed. The rates are shown in Table 1:

Table 1 Optimum Alcohol-Acid Ratio Determination

Alcohol-Acid Molar Ratio	1:2	1:2.5	1:3	1:3.5
Esterification Rate%	27.24%	30.04%	68.73%	53.26%

From Table 1, it can be concluded that butyl acetate rates first increased then decreased as acid-alcohol molar ratio increased, and the optimum alcohol-acid molar ratio was determined as 1:3, in which the esterification rate was maximum.

2.2 Catalyst Amount Selection

Alcohol-acid molar ratio was consistently 1:3, water-carrier agent 3 mL, reaction time 60 min, only with catalyst amount changed. The rates are shown in Table 2:

Table 2 Optimum Catalyst Amount Determination

Catalyst Amount (g)	0.2	0.4	0.6
Esterification Rate%	28.38%	68.73%	57.73%

From Table 2, it can be concluded that low catalyst amount brought about low butyl acetate rate, and that 0.4 g catalyst amount produced maximum esterification rate, which however decreased with the increase of catalyst amount. This comes possibly from side reaction increase caused by catalyst increase, and result in decreased esterification rate. Considering this experiment, the optimum catalyst amount was determined as 0.4 g.

2.3 Reaction Time Selection

Alcohol-acid molar ratio was consistently 1:3, catalyst amount 0.4 g, water-carrier agent 3 mL, only with reaction time changed. The rates are shown in Table 3:

Table 3 Reaction Time Determination

Reaction Time(min)	60	90	120	150
Esterification Rate%	68.73%	72.93%	80.83%	78.32%

From Table 3, it can be concluded that esterification rate increased as the reaction time increased, then decreased after reaching an apex. The optimum reaction time was determined as 120 min.

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 1:3, catalyst amount 0.4 g, reaction time 120 min, only with water-carrying agent amount changed. The rates are shown in Table 4:

Table 4 Optimum Water-Carrying Agent Amount Determination

Water-Carrying Agent Amount(mL)	3	4	5	6
Esterification Rate%	74.19%	80.83%	93.50%	76.53%

From Table 4, it can be concluded that esterification rate was maximum using 5mL of methylbenzene, addition or subtraction of which should decrease esterification rate. This is possibly induced by the reversibility of esterification. Water-carrying agent in small amount can bring out generated water from reaction, but in excessive amount, not only does it decrease the concentrations of alcohol and acid, but also decrease overly the reaction temperature. Optimum water-carrying agent amount was thus determined as 5 mL.

2.5 Parallel Experiments on Optimum Condition

Reaction time was consistently 120 min, alcohol-acid molar ratio 1:3, catalyst amount 0.4 g, water-carrying agent amount 5 mL. The rates are shown in Table 5:

Table 5 Parallel Experiments on Optimum Condition

Parallel Experiments	1	2	3
Esterification Rate%	92.70%	93.50%	91.60%

2.6 Catalyst Reusability

On optimum condition determined by the above experiment, catalyst reusability was investigated and shown in Table 6.

Table 6 Catalyst Reusability

Catalyst Reuses	1	2	3	4	5
Esterification Rate (%)	93.50	88.13	84.12	78.14	70.33

From Table 6, it can be concluded that catalyst activity decreased as it was reused. The rate of 70.33% after reused 5 times indicates that this catalyst has a high stability and can be repeatedly used on such condition.

2.7 Product Analysis

The butyl acetate from this experiment was colorless liquid with fruit-like scent. The refractive index measured $n\ D^{20} = 1.3953$, and standard refractive index of butyl acetate is $n\ D^{20} = 1.3951$.

CONCLUSION

The optimum condition of butyl acetate synthesis with catalysis by Waugh structure $(NH_4)_6[MnMo_9O_{32}]8H_2O$ is: alcohol-acid molar ratio 1:3, catalyst amount 0.4g, water-carrier agent 5 mL of methylbenzene (total volume of reaction system: 23 mL), zeolite about 10 granules, reaction time 120 min, selectivity 100%. Maximum esterification rate was 93.50%.

Butyl acetate synthesis with catalysis by molybdenum-manganese polyoxometalate is characterized by high conversion rate, perfect selectivity, less pollution, catalyst reusability, no discharge of waste acid, undemanding processes and posttreatment, etc., which render it a promising, environment-friendly catalyst.

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