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Research Article

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Synthesis of ethyl acetate catalyzed by $(NH_4)_6[MnMo_9O_{32}].8H_2O$ with Waugh structure

Yuan Hua, Fan Xiaozhen and Zuo Shaoqing

College of Chemistry and Chemical Engineering, Cangzhou Normal University, Cangzhou, Hebei, China

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ABSTRACT

$(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$ with Waugh structure was used as a catalyst for synthesizing ethyl acetate. Control variate method was adopted to determine reaction conditions. Optimum conditions determined by experiment: acid alcohol mole ratio was 3.0:1; 0.3g catalyst and 3ml water-carrying reagent were used; reaction time was 2.0h; selectivity was 100%; conversion rate reached 91.36%.

Keywords: Waugh structure, catalysis, synthesis, ethylacetate

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INTROUDUCTION

Ethyl acetate is an important chemical raw material, excellent organic solvent and diluents, and is widely applied in synthesis of dyestuffs, drugs and perfumes etc[1]. For a long time, industrial production of ethyl acetate has been catalyzed by concentrated sulfuric acid, which entails severe corrosion, many side reactions and complicated process and causes a great deal of acid-containing wastewater. With increasingly stringent international environmental protection laws, seeking inexpensive, easily recyclable, reusable environmentally friendly green catalysts with low catalytic amount will become future development trend. Heteropolyacid is very strong Bronsted acid and serves as acid catalyst; compared with traditional mineral acid, it is used at low level, does not corrode equipments and is free from pollution and reusable etc. In recent years, relevant researches[2-5] have mostly focused on heteropoly anion aspects including Keggin type, Dawson type and Anderson type etc, while researches on catalysis enabled by Waugh type heteropoly anion is still at the initial stage. In this paper, the author synthesized $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$ with Waugh structure and adopted it as catalyst for conducting catalysis research on synthesis of ethyl acetate.

EXPERIMENTAL SECTION

1.1 Instruments and reagents

32 type-middle organic chemical preparation device (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 infrared analyzer (Japanese Shimadzu Corporation).

Glacial acetic acid, absolute ethyl alcohol, sodium chloride solid, sodium carbonate solid, anhydrous magnesium sulfate, benzene, methylbenzene, cyclohexane etc (analytically pure).

1.2 Test method

1.2.1 Preparation of catalyst

Weighed certain amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ to be dissolved in certain amount of water, used glacial acetic acid to adjust pH as 4˜6, heated it to be boiling; dissolved certain amount of $MnSO_4\cdot H_2O$ in hot water, mixed it with the above solution, stirred and heated it to be boiling, resulting in yellow precipitate; added certain amount of

$(NH_4)_2S_2O_8$ solution, heated solution to become nacarat; placed it under room temperature for several hours, and separated out nacarat crystal, carried out suction filtration and recrystallization for three times, dried it at 70˜80℃, resulting in nacarat crystal which featured rhombus as observed by 5×40 microscope[6-8].

1.2.2 Synthesis of ethyl acetate

Conducted reaction in three-necked bottle with thermometer and water segregator; added glacial acetic acid and absolute ethyl alcohol according to stoichiometric ratio, appropriate amount of catalyst, several zeolites and certain volume of water-carrying reagent, and added certain volume of distilled water in water segregator, heated and refluxed for a certain time. After reaction, poured out liquid and recycled solid catalyst; quietly placed it for layering, washed oil layer with saturated Na_2CO_3 and saturated NaCl solution respectively, dried solid $MgSO_4$ particles and then conducted distillation, collected 73~78℃cut fraction, obtained ethyl acetate.

Took certain amount of mixture, and titrated it with standard NaOH solution, obtained acetic acid residue, calculated ethyl acetate esterification rate according to the following formula:

Esterification rate = (initial amount of acetic acid substance - final amount of acetic acid substance) / initial amount of acetic acid substance × 100%

1.2.4 Selection of acid alcohol mole ratio

In order to increase esterification rate, appropriately excessive amount of relatively inexpensive acetic acid was chosen. Experiment was conducted by changing acetic acid use level under the conditions that 0.3g catalyst and 3mL water-carrying reagent methylbenzene were used and reaction time was 1h; experimental result was shown below:

Table 1 Effects of different acid alcohol mole ratios on yield

Acid alcohol mole ratios	0.5:1	1.0:1	1.5:1	2.0:1	2.5:1	3.0:1	3.5:1	4.0:1
Esterification rate（%）	4.34	14.60	24.38	45.88	63.30	65.85	56.79	52.43

As shown in Table 1, with gradual increase in acid alcohol mole ratio, yield of ethyl acetate increased and then decreased; when acid alcohol mole ratio increased to 3:1, maximum esterification rate was achieved. Thus 3:1 was chosen as acid alcohol mole ratio.

1.2.5 Selection of water-carrying reagent and its use level

1.2.5.1 Selection of water-carrying reagent

As this catalyst is easily decomposed when heated under weak current and aqueous condition[9], 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, acid alcohol mole ratio was 3:1, 0.3g catalyst and 3mL water-carrying reagent were used and reaction time was 1h; experimental result was shown below:

Table 2 Effects of different water-carrying reagents on ethyl acetate yield

Water-carrying reagents	Cyclohexane	Methylbenzene	Benzene
Esterification rate（%）	33.52	65.85	56.87

As shown in Table 2, the same amount of methylbenzene had high water-carrying capacity under the same reaction conditions, thus methylbenzene was chosen as water-carrying reagent.

1.2.5.2 Selection of water-carrying reagent use level

Subject to keeping reaction conditions unchanged and only changing water-carrying reagent use level, relationship between esterification rate and catalyst use level was obtained; result is shown below:

Table 3 Effect of water-carrying reagent use level on ethyl acetate yield

Water-carrying reagent（ml）	2	3	4
Esterification rate（%）	54.59	65.85	47.76

As shown in Table 3, 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.

1.2.6 Selection of catalyst use level

Parallel test was conducted by changing catalyst use level under the conditions that acid alcohol mole ratio was 3:1, and 3mL water-carrying reagent methylbenzene was used and reaction time was 1h; the experimental result was shown in table 4:

Table 4 Effect of catalyst use level on ethyl acetate yield

Catalysis(g)	0.2	0.3	0.4	0.6	0.8
Esterification rate （%）	50.27	65.85	57.63	51.14	41.73

As shown in Table 4, increasing catalyst use level can enhance esterification rate, but when catalyst use level exceeded 0.3g, esterification rate decreased possibly because excessive catalyst may increase side reactions so that yield decreased, thus 3.0g was chosen as catalyst use level.

1.2.7 Selection of reaction time

Relationship between esterification rate and time was obtained by only changing reaction time under the conditions that acid alcohol mole ratio was 3:1, and 3mL water-carrying reagent methylbenzene and 0.3g catalyst use level were used; result was shown in fig 1.

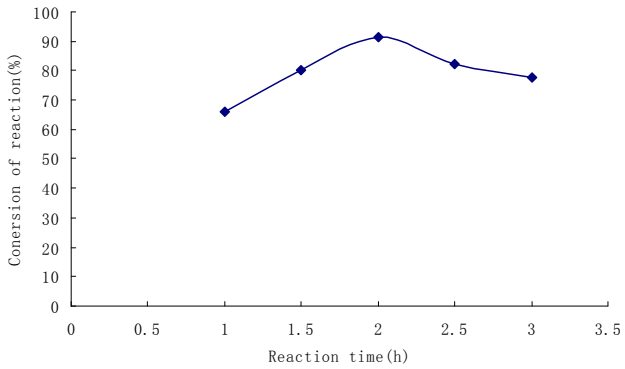

Fig.1Effect of reaction time on ethyl acetate yield

As shown in fig 1 , ethyl acetate yield increased and then decreased with increasing reaction time because esterification reaction is exothermic reaction, and as reaction time increases and reaction system temperature rises, equilibrium constant decreases, reaction equilibrium shifts to hydrolysis of ethyl acetate, resulting in decreasing yield. Therefore, 2h was chosen as reaction time under experimental conditions.

1.2.8 Reusability of catalyst

Reusability of catalyst was examined under optimum conditions obtained in the above experiment[10]; experimental result was shown in fig 2.

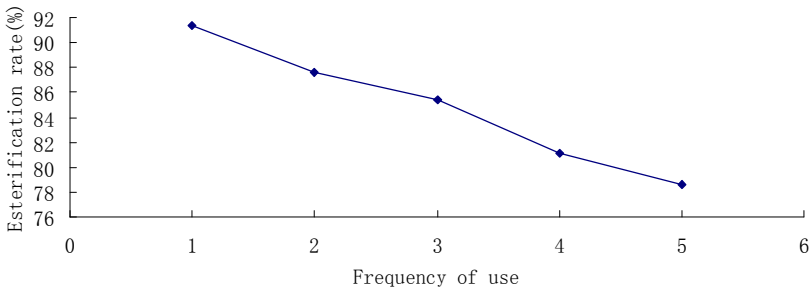

Fig.2 Reusability of catalyst

As shown in fig 2, catalytic activity of catalyst gradually decreased with increasing number of uses, but after catalyst was used for five times, esterification rate was still as high as 78.62%, 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

Experimentally synthesized ethyl acetate is colorless liquid with fruity odor; gas chromatographic method was adopted to conduct selectivity analysis of product; test result only contained ethyl acetate and acetic acid and did not show other impurity peaks, indicating that catalyst was highly selective for catalyzing glacial acetic acid and absolute ethyl alcohol to synthesize ethyl acetate without side reactions. Refractive index of product was measured to be n D^{20} = 1. 3713, consistent with literature value [11]; infrared spectrum detection showed that there was relatively strong C=O stretching vibration absorption peak at 1725 cm^{-1}, and C-O-C characteristic peak at 1239 cm^{-1}, suggesting that synthetic product was ethyl acetate.

CONCLUSION

Research showed that $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$ with Waugh structure was one excellent catalyst for preparing ethyl acetate; optimum process conditions for synthesizing ethyl acetate: acid alcohol mole ratio was 3:1; 0.3g catalyst and 3mL water-carrying reagent methylbenzene were used; reaction time was 2h; ethyl acetate yield can reach 91.36%.

Compared with concentrated sulfuric acid, as a catalyst, $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$ with Waugh structure is characterized by high selectivity, high conversion ratio, easy separation of catalyst, being reusable, no discharge of waste acid etc and is a potential green environmentally friendly catalyst with industrial application prospect.

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