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Research Article

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# Synthesis of iso-amyl acetate using $[(CH_2)_5NH_2]_5BMO_{12}O_{40}$ as catalyst

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## Abstract

Synthesis of iso-amyl acetate using [(CH2)5NH2]5BMO12O40 as catalyst has been studied. Factors influencing the synthesis were discussed. The optimized conditions are: molar ratio of iso-pentanol to acetic acid is 1. 2∶ 1; the quantity of catalyst is equal to 1. 5% of the feed stock, the reaction temperature is 110℃ and the reaction time is 1.5h. $[(CH_2)_5NH_2]_5BM_{O12}O_{40}$ is an excellent catalyst for synthesizing iso -amyl acetate with high yield o f 95. 3% .

**Keywords:** $[(CH_2)_5NH_2]_5BMo_{12}O_{40}$ ; Keggin structure ; Catalysis ; iso -amyl acetate.

## Introduction

Isoamyl acetate is a kind of widespread used ester compounds, mainly used as spices and solvent. In industry, isoamyl acetate is made of acetic acid and isoamyl alcohol esterification with concentrated sulfuric acid as catalyst. Sulfuric acid is used as catalyst for the esterification reaction, although the price is low, it has some fatal defects: seriously corrosion equipment and difficulty of product separating.

As a new interdisciplinary subject, polyoxometalates chemistry is playing an increasingly important role in the catalysis, medicine,material science fields[1-2]. Compared with the traditional catalysts, heteropoly acid and its salts have received far attention becaused of unique acidic (i.e. acid strength relatively homogeneous pure B acid), multifunction, reaction field homogeneity and "a pseudo-liquid phase," behavior and other characteristics. Due to heteropoly acid and its salt is a kind of acid, alkali and oxidation reducing both dual functional catalysts, the versatility of catalytic materials become the new target for research.

In the present study, Keggin type coordination $[(CH_2)_5NH_2]_5BM_{O12}O_{40}$ polyoxometalates catalyst was synthesized. The composite catalyst was applied to the synthesis isopentyl acetate from acetic acid and isoamyl alcohol esterification. The influence factors of the reaction were also investigated.

## Experimental Section

$Na_2MoO_4{\cdot}2H_2O$, hexahydropyridine and acetic acid obtained from Shanghai Chemical Reagent Co. Ltd., isoamyl alcohol and $H_3BO_3$ were purchased from Beijing Chemical Reagent Co. Ltd.

### Materials synthesis:

The 20 g $Na_2MoO_4{\cdot}2H_2O$ were dissolved by 40 mL deionized water and kept in boiling water bath for 80 ºC. The 1.0g $H_3BO_3$ were added in the solutions in the conditions120 r/min. In 10 min, the HCl were added into the solutions so that the solution was stable at pH 2.

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After reaction for an hour, the solution was cooled to ambient temperature. After filtered, 3ml 6 M HCl were added into the liquid so that the solution was stable at pH 2. The reaction again proceeds 2 h in the conditions of 120 r/min, 80 ºC. After moved to the separatory funnel, 30 ml ethyl ether was added into the liquid when the solution was cooled to ambient temperature. The mixture oscillated, deflated, at last keep static in 15min. The below solutions were one more extracted with 10 ml water, 30 mlethyl ether and 10ml HCl. The extracted oil phase with added a small amount of distilled water (10-20 drops) and a few drops of concentrated $HNO_3$ were evaporated under the 60 ºC water bath until the films appeared. Then the transparent tungstosilicic acid as attained after cooled. The purity of crystal was obtained with nearly 100 % after recrystallization.

The precipitate was prepared by mixing the 30 ml $H_5BMo_{12}O_{40}\cdot nH_2O$ and hexahydropyridine with mole ratio 1:3 and reaction at 80 ºC for 2 h. After filteration, the precipitate was cleaned by ethanol, ethyl ether and $H_2O$ in order and dissolved in the mixture of the acetonitrile. After filtered, the filtrates were transferred to the beaker and kept at room temperature for several work. The $[(CH_2)_5NH_2]_5BM_{O12}O_{40}$ crystal would crystallize at the bottom of the beaker.

Adding a certain amount f glacial acetic acid isoamyl alcohol, catalyst and 25 milliliters dry benzene (azeotropic agent) in 100-mlliliter three-necked flask, install with a mixer, water segregator, reflux condenser pipe and thermometer, heating ,mixing and refluxing 2 hours. After the reaction, and then filtration, the acidity value was finally determined. According to the transformation of acid, the conversion rates were calculated. The equations is described as 1:

$$Y=1-\frac{W_{ab}}{W_{af}} \times 100\%$$

Y：Esterification yield,
Wab=the mass of acetic acid before esterification
Waf=the mass of acetic acid after esterification

Catalytic activity: The effects of catalyst, reactants, temperature and reaction time were investigated.

## Results and Discussion

The effect of catalyst dosage on the yields of products was shown in Table 1 with other conditions unchanged. The mass ratio of $[(CH_2)_5NH_2]_5BM_{O12}O_{40}$ / reactants was varied from 0.5-2.5%. As can be seen, catalyst dosage significantly affected the reaction. The yield of the isopentyl acetate was promoted with the increase of molar ratio. The increasement range is bigger until the mass ratio reach1.5%.When the molar ratio exceed 1.5%, the yield of the isopentyl acetate decreases slightly. The most beneficial molar ratio of $[(CH_2)_5NH_2]_5BM_{O12}O_{40}$/ reactants was chosen to be1.5%.

Table 1 Catalytic effect of catalyst dosage on the on the yields of products

| Mass fraction of catalyst | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
|---|---|---|---|---|---|
| Yields% | 65.7 | 93.5 | 95.3 | 94.1 | 87.8 |

The effect of acid and alcohol mole ratio on reaction was also studied （Table 2）with other conditions unchanged. The yields of products were promoted with the molar ratio of alcohol /acid when the molar ratio was less than 1.2:1. While above the molar ratio1.2:1, the yield was decreased with the molar ratio of alcohol /acid.

Table 2 The effect of acid and alcohol mole ratio on the on the yields of products

| Acid and alcohol mole ratio | 1.0 | 1.1 | 1.2 | 1.3 | 1.4 |
|---|---|---|---|---|---|
| Yields% | 72.3 | 89.7 | 95.3 | 92.4 | 86.6 |

The effect of reaction temperature on the reaction was investigated with other conditions unchanged. Table 3 showed the effect of the temperature on the yields of product. It can be observed that temperature have a significant effect on the reactions. When the reaction temperaturereach 110ºC, there was a significant increase in the yield of isoamyl acetate. When the reaction temperature rose above 80 ºC, the yield of isoamyl acetate began to fall due to unwanted side reactions appeared. Thus the reaction temperature was set to 110 ºC in this experiment.

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Table 3 The effect of reaction temperature on the yields of products

| Temperature(℃) | 70 | 80 | 90 | 110 | 120 |
|---|---|---|---|---|---|
| Yields% | 63.5 | 72.6 | 78.4 | 95.3 | 83.0 |

Time course of esterification was shown in Table 4. The amount of isoamyl acetate grew very fast for the first 2.5 h. Then it was observed slightly to decrease. It was found that 1.5 h were sufficient for completion of the esterification reaction.

Table 4 The effect of reaction time on the yields of products

| Time (h) | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
|---|---|---|---|---|---|
| Yields% | 88.5 | 91.2 | 78.4 | 95.3 | 83.0 |

Under the best conditions, the catalyst repeated use effect was investigated. The catalyst was filtrated and separated after the first reaction. The catalyst was activated for 3 h at 350 ℃ with adding the same alcohol/acid mole ratio of reactants, the result as above seen in table 5. Table 5shows that the catalyst after regeneration has no effect on the yield of products, so the catalyst can be repeated use after regeneration.

Table 5 The effect of repeated times of catalyst on the yields of products

| Repeated times of catalyst | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Yields% | 95.1 | 94.7 | 95.2 | 95.0 | 94.8 |

## Conclusion

From what have mentioned above, we can see clearly that $[(CH_2)_5NH_2]_5BMO_{12}O_{40}$ has great influence on the process of synthesis iso-amyl acetate. Molar ratio of iso-pentanol to acetic acid is 1. 2： 1; the quantity of catalyst is equal to 1. 5% of the feed stock, the reaction temperature is 110℃ and the reaction time is 1.5h. Under the optimum conditions, the yield of the product is above 95%.

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