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Synthesis of iso-amyl acetate using $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ as catalyst

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Abstract

Synthesis of iso-amyl acetate using $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ 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. 3∶ 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. $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ is an excellent catalyst for synthesizing iso -amyl acetate with high yield o f 93.5 % .

Keywords: [(CH2)5NH2]3PW12O40 ; 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 because 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 $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ 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

$Na_2WO_4{\cdot}2H_2O$, hexahydropyridine and benzaldehyde obtained from Shanghai Chemical Reagent Co. Ltd., H_2O_2 (30 %), H_3PO_4 (85 %), isoamyl alcohol and H_3BO_3 were purchased from Beijing Chemical Reagent Co. Ltd.

Materials synthesis:

The 20 g $Na_2WO_4{\cdot}2H_2O$ were dissolved by 40 mL deionized water and kept in boiling water bath for 70 ºC. The 2 mL H_3PO_4 were added in the solutions in the conditions of pH 2, 70 ºC, 120 r/min. After 10 min, the $HClO_4$ were added into the solutions. Firstly, the yellow

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deposit emerged. After filtered, the liquid was cooled to ambient temperature. The total reaction times were 2 h. After moved to the separatory funnel, the liquid was extracted with ethylether and 6 mol L^{-1}HCl. The below solutions were one more extracted with ethyl ether and 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 phosphatotungstic acid was attained after cooled. The purity of crystal was obtained with nearly 100 % after recrystallization.

The precipitate was prepared by mixing the $H_3PW_{12}O_{40}\cdot nH_2O$ and hexahydropyridine with mole ratio 1:3 and reaction at 70 ºC for 2 h. After filteration, the precipitate was cleaned by ethanol, ethyl ether and H_2O in order and dissolved in themixture of the acetonitrile. After filteration, the filtrates were transferred to the beaker and kept at room temperature for one week. The $[(CH_2)_5NH_2]_4PW_{12}O_{40}$ crystal would crystallize at the bottom of the beaker.

Adding a certain amount of 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

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$[(CH_2)_5NH_2]_4PW_{12}O_{40}$ / reactants was varied from0.5-2.5%. As can be seen, catalyst dosage significantly affected the reaction. The yield of the b 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%,t he yield of the isopentyl acetate decreases slightly. The most beneficial molar ratio of $[(CH_2)_5NH_2]_4PW_{12}O_{40}$ / 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	92.5	93.5	92.1	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 1.3:1. 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%	69.8	86.3	91.3	93.5	83.6

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 temperature reach 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.

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

Temperature(℃)	**70**	**80**	**90**	**110**	**120**	**130**
Yields%	64.5	73.8	57.6	91.3	93.5	90.1

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Time course of esterification was shown in Table 4. The amount of isoamyl acetate grew very fast for the first 2h. 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%	76.6	84.2	93.5	86.6	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 5 shows 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%	93.5	92.7	93.2	93.0	91.8

Conclusion

From what have mentioned above, we can see clearly that $[(CH_2)_5NH_2]_4PW_{12}O_{40}$ has great influence on the process of synthesis iso-amyl acetate. Molar ratio of iso-pentanol to acetic acid is 1. 3： 1; the quantity of catalyst is equal to 1. 5% of the feed stock, the reaction temperature is 120℃ and the reaction time is 1.5h. Under the optimum conditions, the yield of the product is above 93.5%.

References

[1] Nakaga Moa Y , Kamata K. , Kotani M, et al. Polyoxovanadometalate-Catalyzed Selective Epoxidation of Alkenes with Hydrogen Peroxide Ange Mo Chem Int Ed,**2005**,44(32):5136-5141.

[2] C J Jiang , A Lesbani, R KaMoamoto, et al. Channel-Selective Independent Sorption and Collection of Hydrophilic and Hydrophobic Molecules by $Cs_2[Cr_3O(OOCC_2H_5)_6(H_2O)_3]_2[\alpha\text{-}SiW_{12}O_{40}]$ Ionic Crystal. J Am Chem Soc**, 2006**, 128(44):14240-14241.

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