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Research Article

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Epoxidation of fatty acid Methyl Esters Catalyzed by $[(CH_2)_5NH_2]_5BMO_{12}O_{40}$ Catalyst

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Abstract

The action of the title catalyst with H_2O_2 leads to a formation of homogeneous phase and an accelerated reaction rate. The catalyst will precipitate in solid particles with the consumption of H_2O_2 and the decreasing temperature, its recovery is up to 90% and catalytic activity is almost unchanged after six consecutive uses. The effect of reaction conditions on the epoxidation and H_2O_2 utilization was investigated. Under the conditions of reaction time 2.5h,catalyst 0.3g, stepwise addition of 30%H_2O_2 3.5（30.88 mmol, reaction temperature 65 ℃,1,2-dichloroethane 20 mL, FAMEs 5.0（22.84 mmol double bond, the product epoxy value is up to 5.78%,double bond epoxidation selectivity 81.9% and H_2O_2 utilization 86%.

Keywords: fatty acid methyl ester; epoxidation; phase transfer catalysis; hydrogen peroxide; phosphotungstic heteropoly acid.

Introduction

Epoxy fatty acid methyl ester (EFAMEs) is a non-toxic plasticizer which is used to process polyvinyl chloride (PVC). The existing process caused a large number of formic acid waste water discharge, and poor color products, epoxy value and H_2O_2 utilization rate is low. This is due to the peracetic acid peroxide which is formed formic acid (acetic acid) and hydrogen peroxide H_2O_2.With the increased awareness of environmental protection and efficient utilization of resources, developing new catalytic system and cleaning process, improve the quality of the products is very urgent.

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 $[(CH_2)_5NH_2]_5BMO_{12}O_{40}$ polyoxometalates catalyst was synthesized. The prepared catalyst catalyzes epoxidation of fatty acid methyl ester, and the process conditions are optimized. The influence factors of the reaction were also investigated.

Experimental Section

Na2MoO4•2H2O, 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 Na2MoO4•2H2O 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. 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 $H_5BMo12O_{40}$•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 H2O 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 $[(CH_2)_5NH_2]$ $_5BMO_{12}O_{40}$ crystal would crystallize at the bottom of the beaker.

Results and Discussion

Effect of reaction conditions on epoxidation and H_2O_2 utilization

The effect of seven factors on the epoxidation of fatty acid methyl ester were investigated by orthogonal experiment. The results showed that the reaction time was 2.5 h, the amount of catalyst was 0.3 g, the content of H_2O_2 (30%) and 5 g of fatty acid methyl ester (H_2O_2 and C = C molar ratio), the reaction temperature was 65 ℃, the dosage of dichloroethane was 20 mL, H_2O_2 was added in one time, 1. 4: 1), the epoxy value of the product is up to 5. 78% .Effects of various factors on epoxy value and H_2O_2 utilization are shown in Fig.1 and Fig.2.

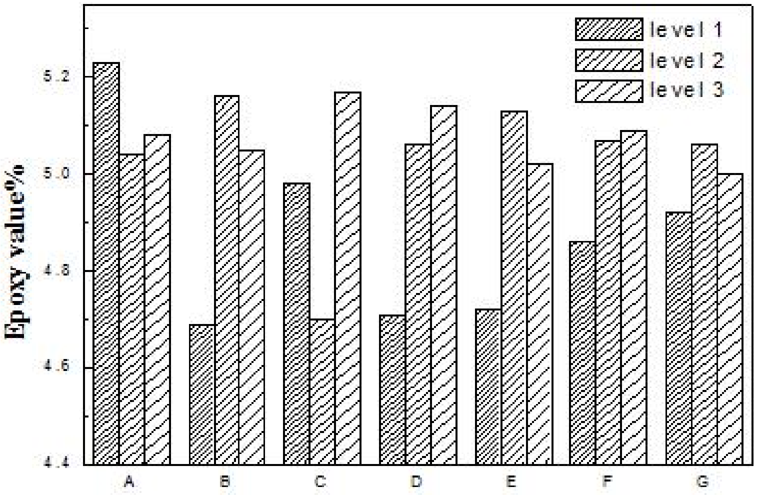

Fig.1 Effect of reaction conditions on epoxy value

A: H_2O_2 added times (1,2,3); B: H_2O_2 and double bond ratio (0. 8∶1 mo l /mo l , 1. 4∶1mo l /mo l , 2∶1mo l /mo l);C: 1, 2 dichloroethane(10 mL , 15 mL , 20 mL); D:reaction ti me (0. 5h , 1 h , 2. 5 h); E: temperature (60 ℃, 65 ℃, 70 ℃); F: H_2O_2 concentration(10%, 20%, 30%);G:catalyst (0. 15 g , 0. 3 g , 0. 5g)

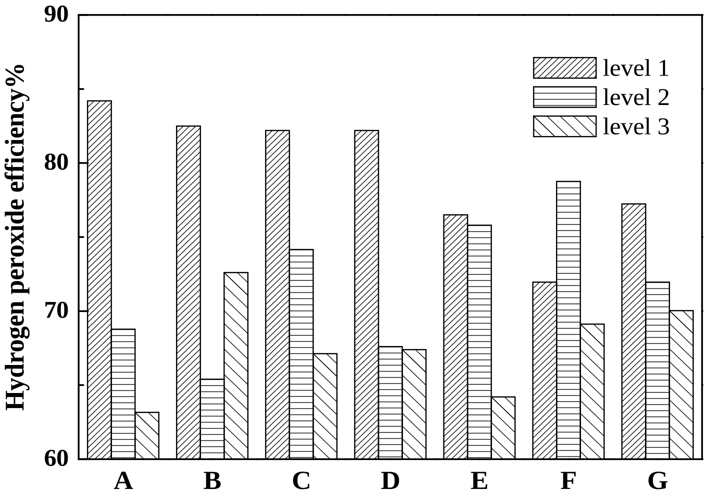

Fig.2 Influence of each factor to H_2O_2 utilization
A:H_2O_2 and double bond mol ratio (0.8∶1, 1.4∶1, 2∶1); B: catalyst (0.15 g, 0.3g, 0.5g); C:reaction time (0.5h, 1h, 2.5h); D:H_2O_2 concentration (10%, 20%, 30%);E:temperature(60 ℃, 65 ℃, 70 ℃); F:1, 2-dichloroethane (10mL, 15 mL, 20 mL);G:H_2O_2 added times(1, 2, 3)

In contrast to formic acid catalyzed epoxidation, H_2O_2 was added into the heteropolyacid phase transfer catalyzed epoxidation process, which resulted in a decrease in the epoxide number of the product, possibly due to the high concentration of H_2O_2, $H_2O_2$is diluted by water in the reaction system, which is not conducive to the epoxidation reaction which is closely related to the ternary ring formation of tungsten oxygen. With the addition of 30% and 20% % H_2O_2, the epoxy value of 10% H_2O_2 is obviously lower than that of 10% H_2O_2. Therefore, in order to get the products with higher epoxy value, the total amount of H_2O_2. The H_2O_2 concentration is sufficiently high (greater than 20%).

The selectivity of epoxidation is 83. 75%, 81. 93% and 71. 58%, respectively, when the molar ratio of H_2O_2 to double bond is 0. 8: 1, 1.4: 1 and 2: H_2O_2 and the double bond molar ratio of 1.4: 1, the epoxy value is high when the H_2O_2 and the double bond molar ratio of 2: 1, epoxidized selectivity of only 71. 58%.The reason described as followed: the large amount of antioxidant H_2O_2will bring the water into the process which promote the epoxy methyl ester hydrolysis reaction, while epoxidation selectivity decreased.

When the amount of solvent is 20 mL or 10 mL, the epoxy value of the product is higher, and the amount of solvent is 15 mL, the epoxy value was lowest. The epoxidation was completed within 2.5 h in the presence of solvent dichloroethane. The epoxidation time needed more than 6 h without using solvent dichloroethane. With the extension of epoxidation reaction time, the hydrolysis of epoxy groups and the degree of dimerization of fatty acid methyl esters gradually increased, and the color deepth of the products increased.

The high temperature resulted in the increasing the decomposition rate of H_2O_2, the lower temperature was of no advantage to the reaction of epoxidation. 65 ℃ was proved a more suitable temperature. The amount of catalyst increased from 0. 3 g to 0. 5 g, the epoxy value did decrease instead of increased. It was suggested that the epoxidation rate of the catalyst was suitable when the amount of catalyst is 0. 3 g. The further increase in the amount of catalyst will give rise to increase the decomposition rate of H_2O_2, however which is not conducive to increase the value of epoxy products. Several factors on the general rule of epoxy value are discussed above, factors on the H_2O_2 utilization are discuseed in the next part.

The experiment proved that the H_2O_2utilization decreases with the increase of H_2O_2 amount. H_2O_2 is consumed by the reaction instead of decopostion, when H_2O_2 is not enough for the double bond. With the increase of H_2O_2 amount, the decomposition of H_2O_2 at the reaction temperature cannot be neglected, which leads to the decrease of the utilization of H_2O_2 and the lower the utilization time of H_2O_2 When the catalyst dosage is 0. 15 g, the utilization rate of H_2O_2 is the highest, and the utilization rate of H_2O_2 is the lowest when the amount of catalyst is 0. 30 g. The influence of catalyst on the utilization of H_2O_2 is different from the influence on epoxy value.

The results show that the amount of H_2O_2 is not only affected by H_2O_2 decomposition and coupled with the catalyst. When the catalyst dosage is less than the optimum amount, the epoxidation reaction rate is low, the decomposition amount of H_2O_2 is increased with the catalyst dosage. However, the amount of H_2O_2 consumed by the epoxidation is cut down so that the utilization of H_2O_2 is decreased. When the amount of catalyst is above the optimum amount, the utilization of H_2O_2 is increased, which indicates that the the heteropoly acid catalytic H_2O_2 decomposition rate and the reaction rate of activating the double bond. Moreover, epoxidizing is more suitable, the utilization rate of H_2O_2 is increased and the epoxy value of the product is raised.

When the H_2O_2 concentrations are of 20% and 30%, the utilization rates of H_2O_2 are similar. When H_2O_2 concentration is 10%, H_2O_2 utilization is highest. Higher concentration of H_2O_2 is conducive to the formation of peroxotungstate groups and promote the depolymerization of the catalyst. At the same time it will accelate the dissolve the catalyst and decomposition of H_2O_2. When the H_2O_2 concentration is less than 10%,the solubility of the catalyst in water is low and the catalyst cannot effectively generate the ternary ring of tungsten and oxygen. While utilization rates of H_2O_2 is higher, the epoxidation activity and epoxy value is reduced. H_2O_2 mass fraction of epoxy products and H_2O_2 utilization rate of the data can be seen as in Table 1. It can be obtained that the process has a high epoxy value even when the H_2O_2 concentration is at 10% indicating that phosphorus tungsten heteropoly acid phase transfer catalyst can effectively use in low concentrations of H_2O_2, reduce the concentration of H_2O_2 in wastewater and decrease production costs.

Table1 Utilization of different H_2O_2 concentrations

H202 concentration %	Epoxy value %	H_2O_2 Eddicienty %
30	4.7653	0.6766
25	5.1235	0.7352
20	4.8988	0.6740
15	5.1321	0.7465
10	4.5668	0.8221

∗catalyst3.197 g, dichloroethane15 mL, catalyst0.3 g, H_2O_2 3.5 g, methylester7

Catalyst recovery performance

The influences of several factors on catalysts recovery is shown in Fig. 3. The conditions are 5 g of methyl ester, 20 mL of dichloroethane, 70 ℃ of temperature and 0. 4 g of catalyst.

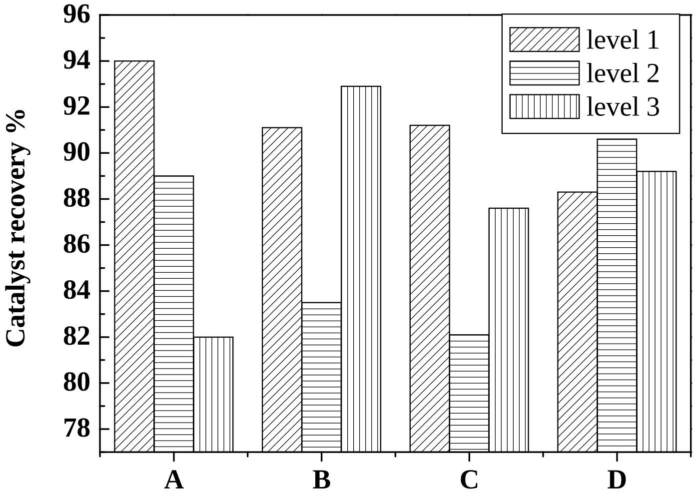

Fig.3 Effect of various factors on catalyst recovery
A: reaction time (0. 5 h , 1 h , 1. 5 h); B:amount of H_2O_2 (1.5g , 2g , 2.5g);C: H_2O_2 added times(1, 2, 3); D:concentration of H_2O_2 (10%, 20%, 30%)

The results showed that the reaction time had the most significant effect on the recovery rate of the catalyst. The reaction time was 0.5 h, the yield of the catalyst was up to 94%, and the recovery rate decreased rapidly with the reaction time prolonged. When the reaction time was 1.5 h, The recovery rate is only 82% . H_2O_2 dosage of 1.5g and 2.5g, the catalyst recovery were 90.5% and 92.3%; H_2O_2 dosage of 2g, the recovery was only 83% The recovery of H_2O_2 was 90.2% and 88%, respectively, and the addition of $H_2O_2$was the same as that of H_2O_2. , The recovery was 82.7% . H_2O_2 concentration of 10%, 20% and 30%, the catalyst recovery of 88% to 91%.

Catalyst recycling performance

The influences of several factors on catalysts recovery is shown in Table 2 under the experimental conditions: fatty acid methyl ester 5g, dichloroethane 20mL, reaction time 0.5 h, 10% H_2O_2 4.5g and catalyst 0.4g. In the case of completion of the reaction, the fresh catalyst was added to the recovered catalyst to make up to 0.4g, and the epoxidation was continued. As can be seen from Table 2, the epoxy value of the catalyst after 6 times reused showed almost no change, indicating good catalyst reusability.

Table 2 Cyclic performance of the catalyst

Entry	Used catalyst/g	Catalyst/g	Epoxy value
1	0	0.40	3.56
2	0.21	0.19	3.76
3	0.24	0.15	3.71
4	0.16	0.26	3.60
5	0.19	0.21	3.32
6	0.18	0.22	3.59

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 epoxidation of fatty acid methyl ester. The catalyst was used to catalyze the epoxidation of fatty acid methyl ester and the consumption of H_2O_2. The optimized conditions are: the reaction time 2.5 h, the amount of catalyst was 0.3 g, and the catalyst was precipitated in 30% H_2O_2 in three times. The recovery rate was 90% and the activity was basically unchanged after repeated 6 times of reaction. The reaction temperature was 65 ℃, the solvent volume was 20 mL, and the fatty acid methyl ester was 5.0 g (containing double bond 22. 84 mmo l). Epoxidation, the product epoxy value of up to 5. 78%, double bond epoxidation selectivity of 81.9%

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