Epoxidation of fatty acid Methyl Esters Catalyzed by 
\[(\text{CH}_2)_5\text{NH}_2\]_5\text{BMO}_{12}\text{O}_{40}\] Catalyst

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Abstract
The action of the title catalyst with \(\text{H}_2\text{O}_2\) leads to a formation of homogeneous phase and an accelerated reaction rate. The catalyst will precipitate in solid particles with the consumption of \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\) utilization was investigated. Under the conditions of reaction time 2.5h, catalyst 0.3g, stepwise addition of \(30\%\text{H}_2\text{O}_2\) 3.5 \((30.88\text{mmol})\), 1,2-dichloroethane 20 mL, FAMES 5.0 \((22.84\text{mmol})\) double bond, the product epoxy value is up to 5.78%, double bond epoxidation selectivity 81.9% and \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\) utilization rate is low. This is due to the peracetic acid peroxide which is formed formic acid (acetic acid) and hydrogen peroxide \(\text{H}_2\text{O}_2\). 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 \[(\text{CH}_2)_5\text{NH}_2\]_5\text{BMO}_{12}\text{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 \(\text{H}_3\text{BO}_3\) 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 °C.
The 1.0g H₃BO₃ were added in the solutions in the conditions 120 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 ml ethyl 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 HNO₃ 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 H₅BMo₁₂O₄₀•nH₂O and hexahydropyridine with mole ratio 1:3 and reaction at 80 ºC for 2 h. After filtration, 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 [(CH₂)₅NH₂]₅BMO₁₂O₄₀ crystal would crystallize at the bottom of the beaker.

**Results and Discussion**

**Effect of reaction conditions on epoxidation and H₂O₂ 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 H₂O₂ (30%) and 5 g of fatty acid methyl ester (H₂O₂ and C = C molar ratio), the reaction temperature was 65 ºC, the dosage of dichloroethane was 20 mL, H₂O₂ 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 H₂O₂ utilization are shown in Fig.1 and Fig.2.

![Fig.1 Effect of reaction conditions on epoxy value](image.png)

A: H₂O₂ added times (1,2,3); B: H₂O₂ 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 ºC, 65 ºC, 70 ºC); F: H₂O₂ concentration(10%, 20%, 30%);G: catalyst ( 0. 15 g , 0. 3 g , 0. 5g )
In contrast to formic acid catalyzed epoxidation, H₂O₂ 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 H₂O₂. H₂O₂ 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% % H₂O₂, the epoxy value of 10% H₂O₂ is obviously lower than that of 10% H₂O₂. Therefore, in order to get the products with higher epoxy value, the total amount of H₂O₂. The H₂O₂ 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 H₂O₂ to double bond is 0. 8: 1, 1.4: 1 and 2: H₂O₂ and the double bond molar ratio of 1.4: 1, the epoxy value is high when the H₂O₂ 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 H₂O₂ will 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 depth of the products increased.

The high temperature resulted in the increasing the decomposition rate of H₂O₂, the lower temperature was of no advantage to the reaction of epoxidation. 65 °C 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 H₂O₂, 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 H₂O₂ utilization are discussed in the next part.

The experiment proved that the H₂O₂ utilization decreases with the increase of H₂O₂ amount. H₂O₂ is consumed by the reaction instead of decomposition, when H₂O₂ is not enough for the double bond. With the increase of H₂O₂ amount, the decomposition of H₂O₂ at the reaction temperature cannot be neglected, which leads to the decrease of the utilization of H₂O₂ and the lower the utilization time of H₂O₂ When the catalyst dosage is 0. 15 g, the utilization rate of H₂O₂ is the highest, and the utilization rate of H₂O₂ is the lowest when the amount of catalyst is 0. 30 g. The influence of catalyst on the utilization of H₂O₂ is different from the influence on epoxy value.
The results show that the amount of H$_2$O$_2$ is not only affected by H$_2$O$_2$ 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$_2$O$_2$ is increased with the catalyst dosage. However, the amount of H$_2$O$_2$ consumed by the epoxidation is cut down so that the utilization of H$_2$O$_2$ is decreased. When the amount of catalyst is above the optimum amount, the utilization of H$_2$O$_2$ is increased, which indicates that the the heteropoly acid catalytic H$_2$O$_2$ decomposition rate and the reaction rate of activating the double bond. Moreover, epoxidizing is more suitable, the utilization rate of H$_2$O$_2$ is increased and the epoxy value of the product is raised.

When the H$_2$O$_2$ concentrations are of 20% and 30%, the utilization rates of H$_2$O$_2$ are similar. When H$_2$O$_2$ concentration is 10%, H$_2$O$_2$ utilization is highest. Higher concentration of H$_2$O$_2$ is conducive to the formation of peroxotungstate groups and promote the depolymerization of the catalyst. At the same time it will accelerate the dissolve the catalyst and decomposition of H$_2$O$_2$. When the H$_2$O$_2$ 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$_2$O$_2$ is higher, the epoxidation activity and epoxy value is reduced. H$_2$O$_2$ mass fraction of epoxy products and H$_2$O$_2$ 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$_2$O$_2$ concentration is at 10% indicating that phosphorus tungsten heteropoly acid phase transfer catalyst can effectively use in low concentrations of H$_2$O$_2$, reduce the concentration of H$_2$O$_2$ in wastewater and decrease production costs.

| H2O2 concentration (%) | Epoxy value (%) | H2O2 Efficiency (%) |
|------------------------|-----------------|----------------------|
| 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               |

* catalyst 3.197 g, dichloroethane 15 mL, catalyst 0.3 g, H$_2$O$_2$ 3.5 g, methyl ester, 20 mL of dichloroethane, 70 °C of temperature and 0.4 g of catalyst.

**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 °C of temperature and 0.4 g of catalyst.

![Fig.3 Effect of various factors on catalyst recovery](image)

A: reaction time (0.5 h, 1 h, 1.5 h); B: amount of H$_2$O$_2$ (1.5 g, 2 g, 2.5 g); C: H$_2$O$_2$ added times (1, 2, 3); D: concentration of H$_2$O$_2$ (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 was only 82%. The recovery of H₂O₂ dosage of 1.5g and 2.5g, the catalyst recovery were 90.5% and 92.3%; H₂O₂ dosage of 2g, the recovery was only 83%. The recovery of H₂O₂ was 90.2% and 88%, respectively, and the addition of H₂O₂ was the same as that of H₂O₂. The recovery was 82.7%. H₂O₂ 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% H₂O₂ 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 [(CH₂)₅NH₂]₅BMO₁₂O₄₀ 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 H₂O₂. 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% H₂O₂ 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 °C, the solvent volume was 20 mL, and the fatty acid methyl ester was 5.0 g (containing double bond 22.84 mmol). Epoxidation, the product epoxy value of up to 5.78%, double bond epoxidation selectivity of 81.9%.

### References

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