

Peroxopolyoxotungsten-based Ionic Hybrid as a Highly Efficient Recyclable Catalyst for Epoxidation of Vegetable oil with H₂O₂

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A peroxopolyoxotungsten-based ionic hybrid was synthesized by anion-change of peroxopolyoxometalate (POM) $PW_4O_{24}^{3-}$ with dicationic long-chain alkyl imidazolium ionic liquids. The characterization was conducted by FT-IR, TGA, ¹H-NMR and CHN Elemental analyses. Its catalytic performance was evaluated by the epoxidation of soybean oil with H₂O₂ under solvent-free condition, including testing of organic cations influence, catalytic reusability and reaction conditions. The catalyst was proved to be a highly efficient recyclable catalyst for epoxidation of various vegetable oils with H₂O₂, showing high H₂O₂ utilization efficiency, high catalytic activity, convenient recovery and good reuse ability.

Key Words : Peroxopolyoxometalate, Dicationic imidazolium ionic liquid, Epoxidation, Vegetable oil, Hydrogen peroxide

Introduction

Due to the increasing environmental concerns and petroleum supply severity, the use of biomass as raw material for polymers, chemicals, fine chemicals and fuel applications has become an imperative issue in recent years. In this context, Epoxidized vegetable oils, as one kind of vegetable oils derivatives, play an important role in industry of fine chemicals, which can be used as PVC-plasticizers¹ and polymer stabilizers². Industrially, the epoxidation of vegetable oils is currently carried out by Prileschajew reaction, in which peracids are performed as oxidizing agents together with strong mineral acids as catalysts.³ However, such process caused severe safety and corrosion problems concerning the existence of the peracids.⁴ Therefore, the peracid-free epoxidation of vegetable oils with H₂O₂ came into people's attention.

Currently, various transition metal compounds, such as molybdenum,^{5,6} manganese,⁷ tungsten^{8,9} and rhenium¹⁰ have been investigated as the homogenous catalysts for the epoxidation of vegetable oils. Among which, tungsten-containing polyoxometalates (POMs), typically the Venturello-Ishii $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species, has received much attention for its catalytic effectiveness for the H₂O₂-based epoxidation of alkenes.^{11,12} Excellent activity and selectivity are shown in POMs, yet its recyclability remains an important and challenging goal in reducing the production cost of desired epoxides. To address this issue, the immobilization of POM onto the surface of an inorganic solid support^{13,14} or polymer support^{15,16} is mostly used. Via such, complete separation of the catalyst from the reaction system is proved to be applicable. Nevertheless, it is difficult to retain or raise their activities relative to those of their homogeneous counterparts.

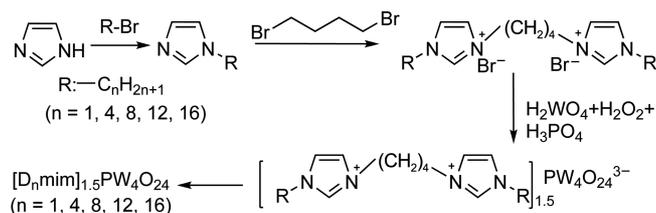
It is recently recognized that the combination of organic

species with POM may cause the formation of organic-POM hybrid with diverse chemical structures and thus improve its catalytic behaviors.¹⁷⁻¹⁹ On the other hand, Ionic liquids (ILs) have been revealed as green reaction media with the properties being flexibly adjusted by various cations and anions.²⁰ Indeed, the combination of IL cations with POM anions has been investigated recently as a new research respect, and some POM-based IL compounds have been synthesized and employed as effective and recyclable catalysts for various organic transformations, and epoxidation of alkenes especially.²¹⁻²³ However, much less work has been dedicated in preparation of POM-based long-chain alkyl imidazolium hybrid, and their potential use as catalysts in the epoxidation of vegetable oils.

In this work, we synthesized a series of POM-based ionic hybrids by combining dicationic long-chain alkyl imidazolium cations with Venturello anions. The hybrids were proved to be highly active and selective recyclable catalysts for epoxidation of vegetable oils with H₂O₂ under solvent-free conditions. The excellent performance can be arise from the dicationic cations that provide the catalyst with solid nature and insolubility, and the long-chain alkyl that facilitate the accessibility of organic oil substrates to the POM active sites.

Experimental

Materials and Methods. The refined soybean oil (SBO) was kindly provided by Hairma Chemicals (GZ) Ltd. Hydrogen peroxide is provided by ARKEMA Hydrogen Peroxide Co., Ltd. Shanghai. Imidazole, 1-bromo-hydrocarbon, *N,N*-dimethylformamide (DMF), sodium hydride, Ethyl acetate (EtOAc) were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All the other chemicals were of analytical reagent grade, which were used



Scheme 1. Typical preparation procedure of the catalysts.

as supplied.

FT-IR spectra were recorded on an ABB FTLA2000 FT-IR spectrometer (Canada) (KBr discs, 4000–500 cm⁻¹). TGA was carried out with a METTLER-TOLEDO TGA/1100SF instrument (Switzerland) in N₂ at a heating rate of 10 °C/min. Elemental analyses (C, H, and N) were performed on a CHN elemental analyzer (Elementar Vario EL III, Germany). The ¹H-NMR spectra were recorded on an AVANCE III 400 MHz digital NMR spectrometer (Bruker, Germany) using a CDCl₃ solvent.

Preparation of Catalyst. The procedure for the synthesis of the catalysts is shown in Scheme 1. The preparation of [D₁₆mim]_{1.5}PW₄O₂₄ is used as an example.

The Synthesis of *N*-Hexadecylimidazole. *N*-Hexadecyl bromide (11.35 g, 37.2 mmol) was dissolved in dimethyl formamide (DMF, 50 mL) and then added to a solution of the sodium salt of imidazole, which was formed by the reaction of imidazole (5.0 g, 74 mmol) with sodium hydride (2.66 g, 111 mmol) in DMF (50 mL). The mixture was heated at 60 °C for 6 h, cooled, and diluted with water. After extraction with ethyl acetate (EtOAc), the extract was washed with brine and water, and then dried with sodium sulfate. The solvent was separated by reduced pressure distillation and *N*-alkylimidazole was obtained as a pale yellow oily product. ¹H-NMR (400 MHz, CDCl₃) δ 7.45 (s, 1H, CH), 7.04 (d, 1H, CH), 6.90 (s, 1H, CH), 3.91 (t, 2H, CH₂), 1.77 (m, 2H, CH₂), 1.27 (m, 26H, CH₂), 0.88 (t, 3H, CH₃).

Dicationic imidazolium ionic liquids were prepared by refluxing *N*-hexadecylimidazole (5.85 g, 20 mmol) and 1,4-dibromobutane (2.16 g, 10 mmol) in isopropanol (50 mL) at 80 °C for 24 h. Then, the products were washed with diethyl ether four times under vacuum. ¹H-NMR (400 MHz, CDCl₃) δ 10.10 (s, 2H, CH₂), 8.07 (s, 2H, CH), 7.27 (s, 2H, CH), 4.58 (s, 4H, CH₂), 4.26 (t, 4H, CH₂), 2.19 (s, 4H, CH₂), 1.91 (d, 4H, CH₂), 1.27 (m, 52H, CH₂), 0.88 (t, 6H, CH₃).

The catalysts were prepared according to Venturello *et al.*²⁴ A suspension of tungstic acid (2.50 g, 10 mmol) in 7 mL of 30% (w/v) aqueous H₂O₂ was stirred and heated at 60 °C until a colorless solution was obtained. After filtering and cooling the solution at room temperature, 40% (w/v) H₃PO₄ (0.62 g, 2.5 mmol) was added and the solution was diluted with 30 mL of water and then stirred for 30 min. 3.00 g of dicationic imidazolium ionic liquid (3.75 mmol) in dichloromethane (40 mL) was added dropwise to the resultant solution with strong stirring over a period of more than 2 min. Stirring was continued for an additional 60 min. The organic phase was then separated, dried over Na₂SO₄, filtered, and gently evaporated by reduced pressure distillation on a rotary

evaporator under reduced pressure at 40–50 °C, which gave a yellow powder. This catalyst was [D₁₆mim]_{1.5}PW₄O₂₄.

Epoxidation Procedure. 10 g SBO and 0.2 g catalyst were added in a 100 mL three-necked flask. The mixture was stirred and heated to a desired temperature. Then H₂O₂ 30% (w/v) was added dropwise to the solution in 30 min and stirred for additional hours. After the reaction, the aqueous phase, organic phase and catalyst were separated by centrifuging, and the organic phase was washed with EtOAc. The solvent was removed by a rotary evaporator under a low vacuum to get epoxidized oils, which were finally dried under vacuum. The catalyst was also washed with EtOAc, centrifuged, dried under vacuum at 45 °C for 2 h, and then reused for the next epoxidation experiment. The conversion, selectivity and yield were calculated as follows:

Conversion % = amount of double bonds converted.

Selectivity % = amount of epoxide formed/amount of double bonds converted.

Yield % = Conversion % × Selectivity %.

Analytical Techniques. The determination of epoxy oxygen group content (EOC) was carried out by the direct method with hydrobromic acid solution in acetic acid. Iodine value was determined by Wijs method (Paquot, 1979). From the oxirane content, the relative conversion to oxirane (RCO) as a percentage was determined using the following formula:

$$\text{Relative conversion to oxirane (RCO)} = (\text{OO}_{\text{ex}}/\text{OO}_{\text{th}}) \times 100$$

where OO_{ex} is the content of oxirane oxygen experimentally determined; OO_{th} is the theoretical maximum oxirane oxygen in 100 g of SBO, which is determined using the following expression

$$\text{OO}_{\text{th}} = [(IV_0/2A_i) / [100 + (IV_0/2A_i) A_0]] \times A_0 \times 100$$

Where A_i (126.9) and A₀ (16.0) are the atomic weights of iodine and oxygen, respectively; IV₀ is the initial iodine value of SBO. The theoretical maximum oxirane oxygen content in 100 g of SBO (OO_{th}) is 7.71%.

Epoxide Analysis. SBO and purified epoxidized soybean oil (ESO) samples were characterized by FT-IR to check whether SBO was converted to ESO (Figure 1). For the IR spectra of SBO in Figure 1, the characteristic peak at 1660 and 3009 cm⁻¹ were respectively attributed to C=C and the C-H stretching of C=C-H in SBO. However, for the IR spectra of ESOs, these peaks disappeared, instead a new peak of 830 cm⁻¹ that was attributed to the epoxy group is observed. Moreover, the intensity of this peak increased when reaction time extended. These results indicate that C=C double bonds in SBO have been successfully converted into corresponding epoxy groups by epoxidation reaction.

To further confirm the structure of the epoxidized product, ¹H-NMR characterization of SBO and ESO were the selected measure (Figure 2). In the ¹H-NMR spectra of original SBO, B, C, D, E, F and H are the peaks associated with the methylene hydrogens of the triglyceride, G is the peak of the methyl hydrogens of the triglyceride, and A is the peak of the olefinic hydrogens and the methine hydrogen of the

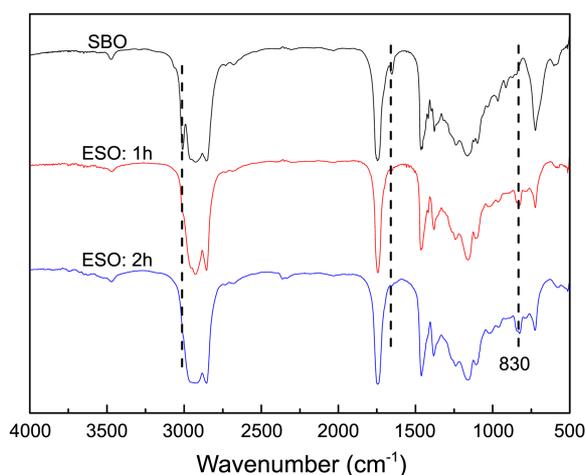


Figure 1. FT-IR of SBO and ESOs.

glycerol moiety, Figure 2(a). As is shown in the characterization result of the products after 2 h of reaction at 80 °C, the formation of epoxide products is proved by from the appearance of hydrogen signals in the 2.9-3.1 ppm region related to the formation of the epoxide group in the $^1\text{H-NMR}$ spectrum (Figure 2(b)). The obviously weakened intensity of the peak (A) could also contribute to this conclusion.

Results and Discussion

Characterization of Catalyst Structure. The FT-IR spectra of the hybrid catalysts are shown in Figure 3. The characteristic bands of the Venturello anion structure $\{\text{PO}_4[\text{WO}(\text{O}_2)_2\text{O}_2]\}_4^{3-}$ appear at 1077 and 1039 (P-O), 942 (W=O), 889 (W-O-W), 852 (O-O), 811 (W-O-W) and 591 cm^{-1} (W-O-O). For all the hybrid samples, featured peaks as well as bands of organic groups can be observed clearly. For example, $[\text{D}_{16}\text{mim}]_{1.5}\text{PW}_4\text{O}_{24}$ has bands at 3145 and 3099 cm^{-1} that can be attributed to the stretching vibration of the C-H bond in imidazole; peaks at 2960, 2918 and 2848 cm^{-1} are due to the stretching vibration of the C-H bond in the alkyl chain; peaks at 1562 and 1464 cm^{-1} that are due to the skeletal

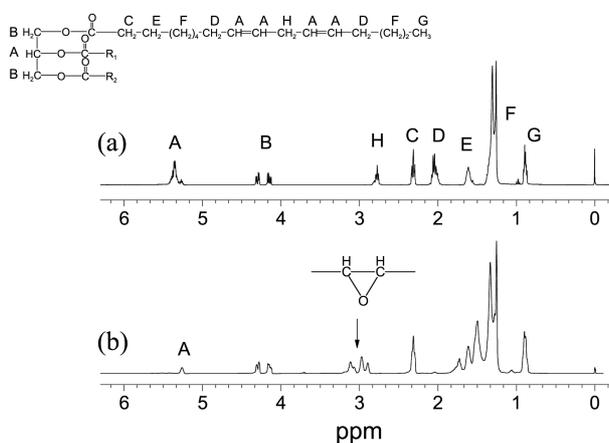


Figure 2. $^1\text{H-NMR}$ spectra of SBO showing: (a) SBO (R_1 and R_2 are alkyl groups), (b) oil epoxidized at 80 °C for 2 h.

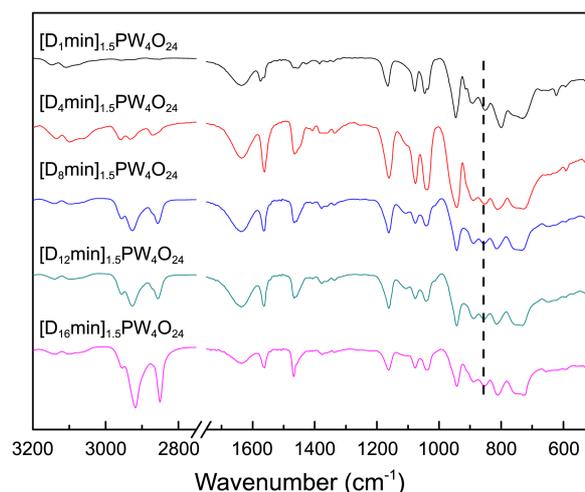


Figure 3. FT-IR spectra of catalysts.

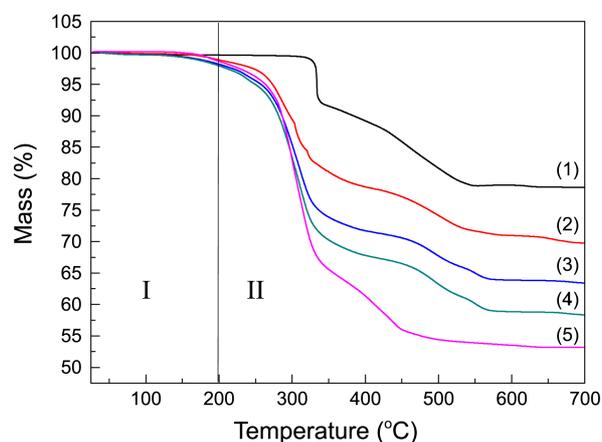


Figure 4. Thermogravimetric curves of catalysts. (1) $[\text{D}_1\text{mim}]_{1.5}\text{PW}_4\text{O}_{24}$; (2) $[\text{D}_4\text{mim}]_{1.5}\text{PW}_4\text{O}_{24}$; (3) $[\text{D}_8\text{mim}]_{1.5}\text{PW}_4\text{O}_{24}$; (4) $[\text{D}_{12}\text{mim}]_{1.5}\text{PW}_4\text{O}_{24}$; (5) $[\text{D}_{16}\text{mim}]_{1.5}\text{PW}_4\text{O}_{24}$.

vibration of the imidazole ring; peaks at 1169 and 1107 cm^{-1} that are due to the stretching vibration of the C-C bond and C-N bond, respectively. These observations confirm that the combination of dicationic alkyl imidazolium organic cations with the Venturello anion via ionic linkage produced a new type of organic POM salt.

The TGA of the catalysts is shown in Figure 4. The hybrids were stable up to 200 °C and yet decomposed rapidly above 250 °C. Notably, the decomposition temperature of $[\text{D}_1\text{mim}]_{1.5}\text{PW}_4\text{O}_{24}$ is higher than 300 °C, indicating a stable catalyst structure. The weight loss between 300-600 °C is due to decomposition of the organic component in the catalyst, which is consistent with the CHN elemental analysis (Table 1). Thus, these results confirm that the hybrids have the chemical formulas shown in Scheme 1.

Catalytic Performance of Different Catalysts. The results using different peroxophosphatotungstate-based hybrids for the epoxidation of SBO with H_2O_2 are shown in Table 2. For the first synthesized catalyst, $[\text{D}_{16}\text{mim}]_{1.5}\text{PW}_4\text{O}_{24}$ (Entry 5) is observed to have a 77.2% conversion and 82.2% selec-

Table 1. Results of CHN elemental analysis

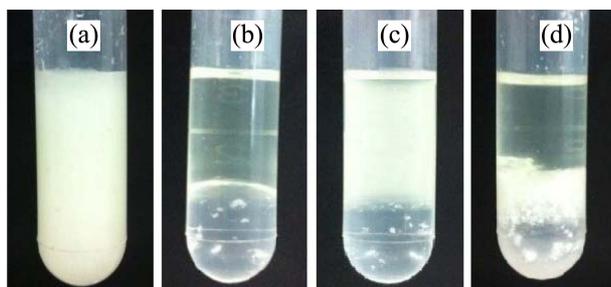
Catalyst	Test value (%) / Theoretical value (%)		
	C	H	N
[D ₁ mim] _{1.5} PW ₄ O ₂₄	14.42/14.60	1.97/2.05	5.66/5.68
[D ₄ mim] _{1.5} PW ₄ O ₂₄	19.97/20.18	3.12/3.02	5.12/5.23
[D ₈ mim] _{1.5} PW ₄ O ₂₄	26.16/26.38	3.98/4.06	4.85/4.73
[D ₁₂ mim] _{1.5} PW ₄ O ₂₄	32.74/31.51	4.72/4.94	4.19/4.32
[D ₁₆ mim] _{1.5} PW ₄ O ₂₄	34.70/35.82	5.32/5.74	3.54/3.98

tivity. Thereafter, a kind of catalyst of different alkyl chain length was synthesized and used as catalyst for this reaction. The results show that the longer of the alkyl chain on the imidazole, the better catalytic activity it has on the epoxidation of SBO. When the carbon chain length was increased from 1 to 12 (Entries 1 to 4), the conversion of SBO increased from 14.9% to 66.6%, while the selectivity of both catalysts was greater than 85%. Possible explanation may be the compatibility of the catalyst has in the oil phase increased with the extension of the alkyl chain, through which the active center of the catalyst could have a better interaction with the SBO. This also gives a reasonable explanation that why [D₁₆mim]_{1.5}PW₄O₂₄ showed the best catalytic activity. More importantly, during the reaction, the catalyst dissolved in the reaction system which caused a homogeneous catalysis. When reaction completed, the catalyst can be self-separated from the SBO phase and dispersed in the oil-water interface (Figure 5). Thus, the catalyst can be separated easily

Table 2. Effect of different catalysts on the epoxidation reaction

Entry	Catalysts	Conversion (%)	Selectivity (%)
1	[D ₁ mim] _{1.5} PW ₄ O ₂₄	14.9	85.1
2	[D ₄ mim] _{1.5} PW ₄ O ₂₄	33.5	84.8
3	[D ₈ mim] _{1.5} PW ₄ O ₂₄	57.8	85.3
4	[D ₁₂ mim] _{1.5} PW ₄ O ₂₄	66.6	86.9
5	[D ₁₆ mim] _{1.5} PW ₄ O ₂₄	77.2	84.2
6	[D ₁₆ mim] _{1.5} PW ₁₂ O ₄₀	–	–

Reaction conditions: 10 g SBO (48.21 mmol double bond), 0.2 g catalyst, 8.20 g 30% H₂O₂, (n(H₂O₂)/n(double bond) = 1.5:1), 60 °C, 4 h.

**Figure 5.** Photographs of the solvent-free epoxidation of SBO with H₂O₂ over the [D₁₆mim]_{1.5}PW₄O₂₄ catalyst: (a) during the reaction (after the addition of H₂O₂), (b) at the end of the reaction: static placed in 60 °C water bath, (c) the catalyst separated at room temperature, (d) the catalyst dispersed in the oil-water interface.**Table 3.** Effect of the catalyst mass ratio on the epoxidation reaction

m (SBO)/m (CAT)	Conversion (%)	Selectivity (%)
100	8.8	86.0
75	56.5	85.4
50	77.2	84.2
25	80.0	78.2

Reaction conditions: 10 g SBO (48.21 mmol double bond), 8.20 g 30% H₂O₂, (n(H₂O₂)/n(double bond) = 1.5:1), 60 °C, 4 h.

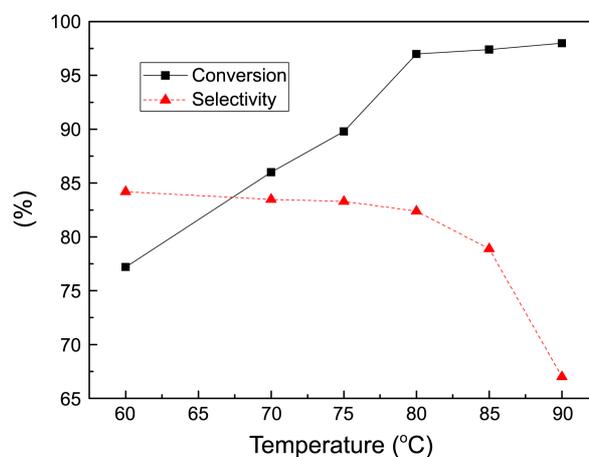
by filtration and reused for the next experiment.

As well known, Keggin POM anion PW₁₂O₄₀³⁻ is a commonly used epoxidation catalyst for various olefins. Here, Keggin heteropoly compounds [D₁₆mim]_{1.5}PW₁₂O₄₀, as a comparison catalyst, was synthesized, which had the identical cation in [D₁₆mim]_{1.5}PW₄O₂₄. However, no catalytic activity was observed under the same reaction conditions (Entry 6). This result proved that the peroxyheteropolyanion act as an active center, which is in consistent with the previous reported research.²⁴⁻²⁷

Effect of the Catalyst Mass Ratio. In order to improve the yield of the epoxides formed under green chemical conditions taking [D₁₆mim]_{1.5}PW₄O₂₄ as the catalyst, several parameters (catalyst mass ratio, temperature, time, H₂O₂ molar ratio, H₂O₂ concentration) were examined.

The effect of mass ratio of the SBO with catalyst (CAT) [D₁₆mim]_{1.5}PW₄O₂₄ was studied at 60 °C (Table 3). It can be seen that by decreasing the SBO/CAT mass ratio, the conversion increased, however, the selectivity decreased. When the SBO/CAT mass ratio was 50, the best catalytic activity was obtained. Therefore, we selected a mass ratio SBO/CAT of 50 in later study.

Effect of Temperature. The influence of the reaction temperature in the epoxidation of SBO with H₂O₂ was investigated (Figure 6). With the increasing temperature from 60 to 90 °C, conversion of SBO increased almost linearly from 77% to 98%, but the selectivity decreased. Dramati-

**Figure 6.** Effect of reaction temperature on the epoxidation reaction. Reaction conditions: 10 g SBO (48.21 mmol double bond), 0.2 g [D₁₆mim]_{1.5}PW₄O₂₄, 8.20 g 30% H₂O₂, (n(H₂O₂)/n(double bond) = 1.5:1), 4 h.

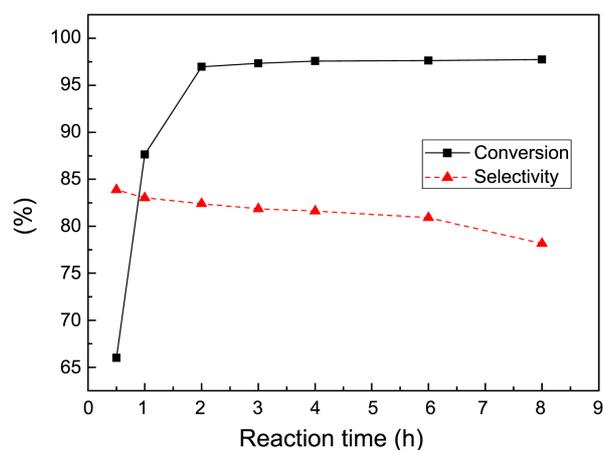


Figure 7. Effect of reaction time on the epoxidation reaction. Reaction conditions: 10 g SBO (48.21 mmol double bond), 0.2 g $[D_{16}mim]_{1.5}PW_4O_{24}$, 8.20 g 30% H_2O_2 , $n(H_2O_2)/n(\text{double bond}) = 1.5:1$, 80 °C.

cally as seen, the epoxide selectivity decreased to 65% at 90 °C, which is at higher temperature, the formation of by-products intensified, leading to the decreasing selectivity of ESO.

Effect of Reaction Time. Figure 7 shows the results for effect of reaction time in the epoxidation of SBO with H_2O_2 . The reaction has been completed in approximately two hours with the conversion of 97%, which indicated the occurrence of a rapid reaction. With increasing of reaction time, conversion slightly increased, but yield slightly decreased, however, these changes could be basically negligible. Since H_2O_2 in this system had been mostly exhausted, as reaction time increased, the conversion remain basically unchanged.

Effect of H_2O_2 Molar Ratio on the Epoxidation. The effect of H_2O_2 /double bond of SBO molar ratio [(1/1) to (3/1)] (Figure 8) was studied at 80 °C. The most preferable result was obtained using a molar ratio of 1.5 giving a conversion and a yield of 97.6% and 79.6%, respectively, and that noticed $[D_{16}mim]_{1.5}PW_4O_{24}$ can lead to a high H_2O_2

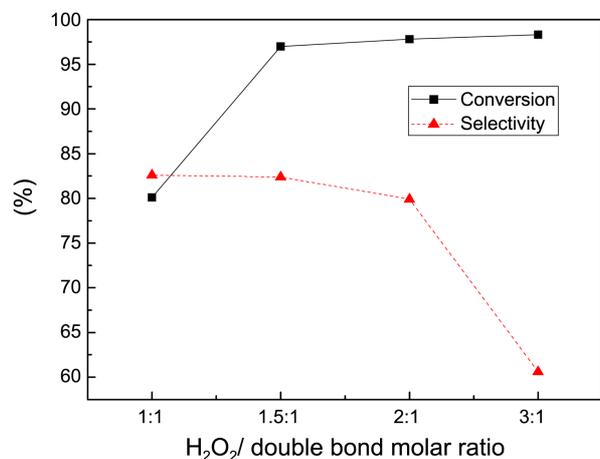


Figure 8. Effect of the oxidant molar ratio on the epoxidation reaction. Reaction conditions: 10 g SBO (48.21 mmol double bond), 0.2 g $[D_{16}mim]_{1.5}PW_4O_{24}$, 80 °C, 2 h.

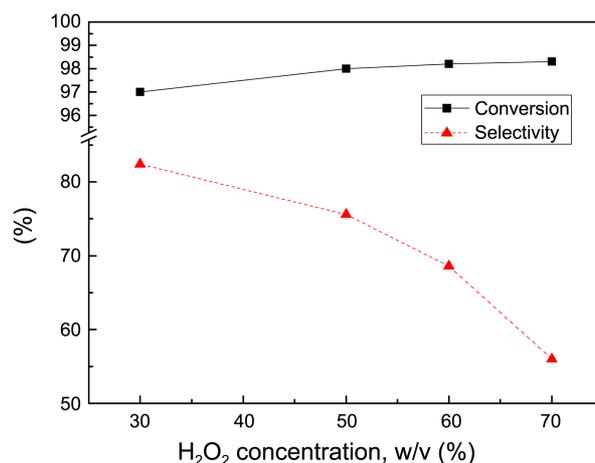


Figure 9. Effect of the concentration of the H_2O_2 . Reaction conditions: 10 g SBO (48.21 mmol double bond), 0.2 g $[D_{16}mim]_{1.5}PW_4O_{24}$, $n(H_2O_2)/n(\text{double bond}) = 1.5:1$, 80 °C, 2 h.

efficiency. It can be concluded that the appropriate excess of H_2O_2 is necessary for its partially decomposition into water and oxygen. However, the excess use of H_2O_2 will aggravate side reaction, leading to ring-opening reaction of the epoxy bond of ESO, which demoted the selectivity and yield.⁵

Effect of the Concentration of the H_2O_2 on the Epoxidation. The effect of the H_2O_2 concentration was studied (Figure 9). The best results were obtained using a H_2O_2 concentration of 30%, w/v. It noticed that the higher concentration of H_2O_2 , the lower selectivity of epoxide products, although the conversion increased slightly. There is a superoxygenation that induces the formation of by-products such as diols or cleavage products due to a stronger oxidation of the substrate with the increase of the oxidant concentration, that is the reason for the decrease of selectivity and yield.⁵

Extrapolation to Other Oils. To investigate the scope of the $[D_{16}mim]_{1.5}PW_4O_{24}$ catalyst for epoxidation reactions, the substrates fatty acid methyl ester, waste oil methyl ester and cottonseed oil were also investigate, and the results are shown in Table 4. All of these substrates were converted into the corresponding epoxides efficiently by using catalyst $[D_{16}mim]_{1.5}PW_4O_{24}$ in solvent-free conditions.

Recycling Tests. The recycling performance of the catalyst $[D_{16}mim]_{1.5}PW_4O_{24}$ was conducted in the epoxidation of SBO (Figure 10). It was observed that the conversions and selectivity were decreased significantly. At the three run tests, the conversion and selectivity were dropped from 97% and 82% to 24% and 20%, respectively. The FT-IR spectra for

Table 4. Catalyst applied in the epoxidation of other oils

Oils	Conversion (%)	Selectivity (%)
soybean oil	97.0	82.4
Fatty acid methyl ester	97.5	83.1
Waste oil methyl ester	95.8	83.5
Cottonseed oil	97.4	81.1

Reaction conditions: 10 g SBO, 0.2 g $[D_{16}mim]_{1.5}PW_4O_{24}$, 8.20 g 30% H_2O_2 , $n(H_2O_2)/n(\text{double bond}) = 1.5:1$, 80 °C, 2 h.

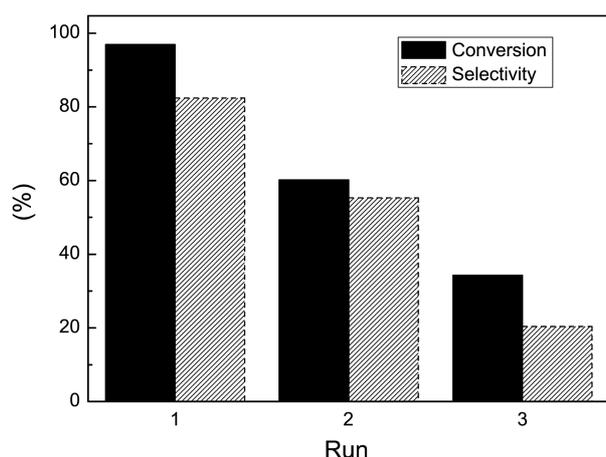


Figure 10. Recycling tests. Reaction conditions: 10 g SBO (48.21 mmol double bond), 0.2 g $[D_{16}mim]_{1.5}PW_4O_{24}$, 8.20 g 30% H_2O_2 , $(n(H_2O_2)/n(\text{double bond}) = 1.5:1)$, 80 °C, 2 h.

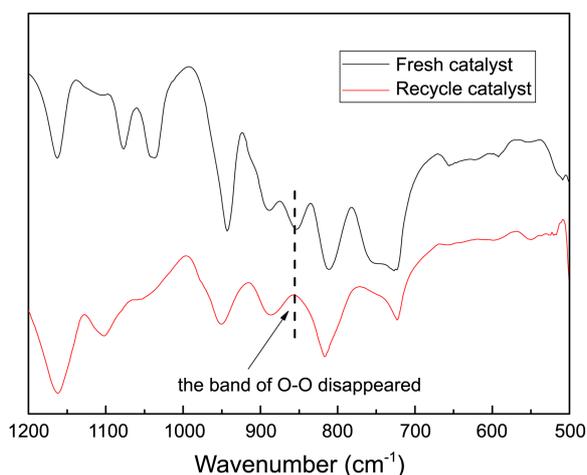


Figure 11. FT-IR spectra of fresh and recycle catalysts.

$[D_{16}mim]_{1.5}PW_4O_{24}$ (Figure 11) showed that the featured peak at 850 cm^{-1} in the fresh catalyst disappeared in the recycled catalyst. This peak has been revealed to be the active site for Venturello-Ishii anions in epoxidation reactions.²⁷ Thus, we think that the disappearance of this active sites may be responsible for the decrease of the recycled catalyst activity. To increase the catalyst's reusability, further research is still required.

Conclusion

In summary, we synthesized the POM-based hybrid material $[D_nmim]_{1.5}PW_4O_{24}$ by the anion-exchange of dicationic alkylimidazolium cation with the peroxopolyoxometalate anion. And $[D_{16}mim]_{1.5}PW_4O_{24}$ was proved to be a highly efficient catalyst for the epoxidation of SBO with H_2O_2 under solvent-free conditions. The excellent performance can be attributed to the dicationic cations that endow the

catalyst with solid nature and insolubility, as well as the long-chain alkyl that facilitate the accessibility of organic oil substrates to the POM active sites. Finally this epoxidation method can be extended to other unsaturated fatty compounds and crude vegetable oils.

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