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Synthesis of Sulfonic Acid-Functionalized Zirconium Poly(Styrene-Phenylvinyl-Phosphonate)-Phosphate for Heterogeneous Epoxidation of Soybean Oil

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Abstract: In this paper, a solid acid catalyst (ZPS–PVPA–SO3H) was prepared by anchoring thiol group on zirconium poly(styrene-phenylvinyl-phosphonate)-phosphate (ZPS–PVPA), followed by oxidation of thiol groups to obtain sulfonic acid groups. The solid acid catalyst was characterized by XPS, X-ray, EDS, SEM, and TG-DSC. The successful preparation of sulfonic acid-functionalized ZPS–PVPA was confirmed. Subsequently, the catalytic performance of ZPS–PVPA–SO3H was investigated in the epoxidation of soybean oil. The results demonstrated that ZPS–PVPA–SO3H can effectively catalyze epoxidation of soybean oil with TBHP as an oxidant. Moreover, there was no significant decrease in catalytic activity after 5 repeated uses of the ZPS–PVPA–SO3H. Interestingly, the ZPS–PVPA–SO3H was kept in 2 mol/L of HCl overnight after the end of the seventh reaction, and the catalytic activity was gradually restored during the eighth to tenth cycles.

Keywords: solid acid; zirconium poly(styrene-phenylvinyl-phosphonate)-phosphate; heterogeneous catalysis; epoxidation of soybean oil

1. Introduction

The epoxidation of vegetable oil has attracted much attention because the obtainable epoxides are useful for producing a wide range of products, such as plasticizers and stabilizers of polyvinyl chloride (PVC) [1]. Currently, these products are mainly prepared by using a peracid [2,3] in the presence of protonic acid catalysts, such as sulfuric acid [4]. However, separation and reuse of such protonic acid catalysts are still problematic for the reaction mixture [3]. In addition, protonic acid catalysts can also pollute the environment, posing a hazard and causing more by-products. Therefore, a new type of effective catalyst is urgently needed for epoxidation of soybean oil.

In the last few decades, a large number of functional catalytic materials containing –SO3H groups have been reported [5–8]. The –SO3H-based functionalized catalytic materials can not only replace liquid acids to catalyze various reactions and reduce wastewater, but also have significant shape-selective catalysis. Their nature also increases the selectivity of the reaction and reduces the by-products of the reaction. Until now, the main choices of catalytic materials have been zeolites, silica,
α-zirconium phosphate, and metal oxides [9–11]. However, –SO$_3$H-based-organic polymer–inorganic hydrogen zirconium phosphate catalytic materials applied to epoxidation of soybean oil have not been reported.

Organic polymer–inorganic hydrogen zirconium phosphate hybrid materials have been central to many areas of chemistry because they have the properties of organic and inorganic ingredients [12,13]. It is mainly because these materials have different hydrophilic or hydrophobic properties (regulating the ratio of organic polystyrene segments to inorganic zirconium hydrogen phosphate components), specific surface areas and holes of different sizes (regulating the ratio of organic polymers), and nanolayer structure. In addition, the surface of the organic polymer–inorganic hydrogen zirconium phosphate also contains a large amount of benzene rings and –OH, which can perform different functionalization reactions.

In our previous works [14,15], the organic polymer–inorganic hydrogen zirconium phosphate, which were frequently functionalized on the benzene ring in the organic component, has been demonstrated to be a versatile support to immobilize the homogeneous chiral Mn$^{	ext{III}}$ (salen) complex. The corresponding works demonstrated that ZPS–PVPA-based catalyst can effectively catalyze α-methylstyrene and indene, especially α-methylstyrene; the conversion and enantioselectivity are 99%. Moreover, the ZPS–PVPA–SO$_3$H catalysts, which were synthesized by the reaction of a chloromethyl group on the benzene ring in ZPS–PVPA and an additional sulfonic acid group, can effectively promote the catalytic epoxidation of soybean oil [16]. However, one of the biggest problems is the use of carcinogenic chloromethyl ether during the functionalization of hybrid materials. In addition, the process was complicated and had a low degree of functionalization.

Hence, the need to better understand these new functionalized hybrid materials and find a more stable, efficient, simple, and reusable solid acid catalyst encourage us to make further efforts. Considering the rich –OH on the surface of ZPS–PVPA and avoiding the use of carcinogenic chloromethyl ether, we extend our attempts to prepare ZPS–PVPA–SO$_3$H by the condensation reaction between the –OH on the surface of ZPS–PVPA and the alkoxyl- or chloro-silane groups of organic molecules. Then, the catalytic performance of ZPS–PVPA–SO$_3$H was investigated in the epoxidation of soybean oil. The results demonstrated that the ZPS–PVPA–SO$_3$H can effectively catalyze epoxidation of soybean oil with TBHP as an oxidant. Moreover, the ZPS–PVPA–SO$_3$H could be easily separated from the reaction system and recycled up to at least five times without significant loss of catalytic activity. Interestingly, ZPS–PVPA–SO$_3$H was kept in 2 mol/L of HCl for overnight and after the end of the seventh reaction, the catalytic activity was gradually restored during the eighth to tenth cycles.

2. Results and Discussion

2.1. The Acidity of the Samples of Solid Particles

The calculated acidities of ZPS–PVPA, ZPS–PVPA–SH and ZPS–PVPA–SO$_3$H are presented in Table 1. The acidity of ZPS–PVPA microcrystals is mainly caused by the –OH within ZPS–PVPA layers [17]. When –SH group terminated chains were grafted onto ZPS–PVPA, the acidity of ZPS–PVPA–SH decreased, indicating the successful condensation reaction between the –OH of individual ZPS–PVPA and the –Si(OMe)$_3$ groups of MPTMS. After the ZPS–PVPA–SH nanosheets were oxidized to ZPS–PVPA–SO$_3$H, the acidity was sharply enhanced to 418.9 µmol/g from 0.12 µmol/g, which in turn confirms the formation of –SO$_3$H groups.

| Number | Sample            | Acidity (µmol/g) |
|--------|-------------------|------------------|
| 1      | ZPS–PVPA          | 7.2              |
| 2      | ZPS–PVPA–SH       | 0.12             |
| 3      | ZPS–PVPA–SO$_3$H  | 418.9            |

Table 1. Acidity of the samples of solid particles.
2.2. X-Ray Photoelectron Spectroscopy

The XPS results for ZPS–PVPA, ZPS–PVPA–SH and ZPS–PVPA–SO₃H are summarized in Figure 1. The appearance of S and Si elements on the surface of ZPS–PVPA–SH confirmed the successful grafting of MPTMS on the ZPS–PVPA. Moreover, the XPS spectra of P 2p for ZPS–PVPA, ZPS–PVPA–SH, and ZPS–PVPA–SO₃H were recorded and are shown in Figure 2. Compared to ZPS–PVPA, the binding energy of the P 2p peak of ZPS–PVPA–SH increased from 134.04 to 134.08 eV after functional reaction. This result is consistent with the formation of –SH groups under the influence of H₂O₂ and HCl, the XPS spectra of S 2p₃/₂ were carried out, and the results are shown in Figure 3. A higher binding energy of S 2p₃/₂ (168.1 eV Vs 163.4 eV) was obtained after the oxidation, which in turns proves that the ZPS–PVPA–SH were successfully oxidized into ZPS–PVPA–SO₃H.

![Figure 1. XPS survey scan of (a) ZPS–PVPA, (b) ZPS–PVPA–SH, and (c) ZPS–PVPA–SO₃H.](image1)

![Figure 2. XPS of P 2p peaks of (a) ZPS–PVPA, (b) ZPS–PVPA–SH, and (c) ZPS–PVPA–SO₃H.](image2)
2.3. XRD Analysis

Figure 4 presents the XRD patterns of ZPS–PVPA, ZPS–PVPA–SH, and ZPS–PVPA–SO3H. It can be seen from the XRD spectrum that there has no obvious peak, indicating that the surface morphologies of the ZPS–PVPA, ZPS–PVPA–SH, and ZPS–PVPA–SO3H are amorphous. The broad peak at 2θ = 15.0–30° is mainly attributed to the amorphous silica. Furthermore, the fine diffraction peaks in ZPS–PVPA, ZPS–PVPA–SH and ZPS–PVPA–SO3H are attributed to the special structure of the organic–inorganic hybrid zirconium phosphate. Theoretically, each of the composite zirconium salt particles is composed of a plurality of layered composite zirconium salt crystallites, and the arrangement of the crystal planes of the respective zirconium salt crystal grains is random. Therefore, the results are very likely to present a form of “short-range order, long-range disorder”.

Figure 3. XPS of S 2p3/2 peaks of (a) ZPS–PVPA–SH and (b) ZPS–PVPA–SO3H.

Figure 4. XRD patterns of solid particles: (a) ZPS–PVPA, (b) ZPS–PVPA–SH, and (c) ZPS–PVPA–SO3H.
2.4. Microscopic Analysis

SEM images provide direct information on the microstructure and morphology of ZPS–PVPA and ZPS–PVPA–SO\textsubscript{3}H, as shown in Figure 5. In this context, Figure 5a indicates that the ZPS–PVPA was amorphous and loose, and various cavities, holes, and pores were present in every particle in ZPS–PVPA. These pores and cavities of varying sizes are caused by the disorderly arrangement of organic polymer and layered crystallites of inorganic zirconium phosphate. Figure 5b shows that the structure of ZPS–PVPA–SO\textsubscript{3}H is still amorphous, loose, and porous. However, compared to ZPS–PVPA, the channels and pores of ZPS–PVPA–SO\textsubscript{3}H are more closely packed, which is mainly due to the insertion of the –SO\textsubscript{3}H group and results in an increase in the interaction between the particles during the sulfonation process. The EDS surveys of ZPS–PVPA and ZPS–PVPA–SO\textsubscript{3}H are presented in Figure 5c,d. The additional peaks of S and Si elements in ZPS–PVPA–SO\textsubscript{3}H further confirm the successful grafting and oxidation of –SH into –SO\textsubscript{3}H group. Furthermore, we carried out element mapping of ZPS–PVPA–SO\textsubscript{3}H (Figure 6a–f). Considerable quantities of Si and S were detected, along with Zr, P, C, and O, implying the successful grafting of MPTMS on the ZPS–PVPA and oxidation of –SH into –SO\textsubscript{3}H group.

![Figure 5](image-url)  
**Figure 5.** SEM photograph of (a) ZPS–PVPA, (b) ZPS–PVPA–SO\textsubscript{3}H, and the measured EDS images of (c) ZPS–PVPA, (d) ZPS–PVPA–SO\textsubscript{3}H.
Figure 5. SEM photograph of (a) ZPS–PVPA, (b) ZPS–PVPA–SO₃H, and the measured EDS images of (c) ZPS–PVPA, (d) ZPS–PVPA–SO₃H.

Figure 6. EDX elementary mapping of (a) C, (b) O, (c) Zr, (d) P, (e) Si, and (f) S in the catalyst ZPS–PVPA–SO₃H.

2.5. Thermal Gravimetric Analysis

The thermal stability of the catalyst ZPS–PVPA–SO₃H was determined by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) (Figure 7). The weight loss of the catalyst ZPS–PVPA–SO₃H is divided into four processes. It can be seen from the TG-DSC curve that the first process is the temperature increase from room temperature to 120 °C, where weight loss occurs at 8.7%, and the corresponding endothermic peak appears at 63.2 °C in the DSC curve, which is attributed to the desorption of surface adsorption water and crystal water in the solid catalyst. The second process was the temperature increase from 155 to 222 °C where a weight loss of 2.9% occurs, which is still due to the removal of residual solid water from the catalyst. The third stage is the temperature increase from 222 to 706 °C, resulting in mass loss of 43.8% and two obvious exothermic peaks occurring simultaneously at 426.3 and 530.4 °C, which is mainly attributed to the decomposition of organic groups and burning of species carbon in the catalyst ZPS–PVPA–SO₃H. Furthermore, the organophosphine is oxidized to pentavalent phosphorus and Zr(HPO₄)₂ is formed at this stage, and the organic group is almost completely destroyed at 706 °C. The fourth stage is the temperature increase from 706 to 800 °C, accompanied by a strong endothermic peak at 667.2 °C. After heating to 800 °C, white residual powder is obtained, which is mainly due to the dehydration of Zr(HPO₄)₂ to form zirconium pyrophosphate.
ZrP2O7. The quality loss is not obvious. From the above thermogravimetric analysis, it can be stated that the thermal stability of the catalyst ZPS–PVPA–SO3H is reached at about 230 °C.

Figure 7. The TG-DSC curves of the ZPS–PVPA–SO3H.

2.6. Catalytic Reaction

Table 2 summarizes the results of the epoxidation of soybean oil over the catalyst ZPS–PVPA–SO3H. All reactions proceeded smoothly, and these results are significantly better than those catalyzed by the Schiff base molybdenum (VI) [18] and the Cu(salen) complex [19] under optimal catalytic conditions. The excellent catalytic activity is mainly attributed to the special structure of ZPS–PVPA–SO3H, which facilitate self-assembly into a plurality of micro-reactors. Thus, the particles of one catalyst are randomly stacked by hundreds of solid catalyst crystallites. The catalytic active centers are typically located in the channels or inner or outer layers of ZPS–PVPA. When the catalyst is in the TBHP oxidation system, the layers of ZPS–PVPA are expanded or even partly decomposed, more secondary channels are formed, and the original secondary channels are enlarged, meaning some of the embed catalytic active sites are exposed in the solution of the reaction and the substrates and the reactants can diffuse to these catalytic sites easily through these secondary channels. As the reaction time raise, the conversion rate increases gradually, but the selectivity decreases accordingly. Similar results were obtained in our earlier reports [13,20].

| Entry | ZPS–PVPA–SO3H (wt%) (h) | Temperature (°C) | Conversion (%) [b] | Selectivity (%) [b] | Yield (%) |
|-------|------------------------|------------------|--------------------|---------------------|----------|
| 1     | 1 (6)                  | 80               | 32.1               | 50.7                | 16.27    |
| 2     | 2 (6)                  | 80               | 53.7               | 57.2                | 30.72    |
| 3     | 5 (6)                  | 80               | 69.1               | 61.6                | 42.57    |
| 4     | 10 (6)                 | 80               | 78.2               | 76.8                | 60.06    |
| 5     | 20 (6)                 | 80               | 81.6               | 73.2                | 59.73    |
| 6     | No catalyst (6)        | 80               | 10.6               | 3.2                 | 0.34     |
| 7     | 10 (6)                 | 40               | 36.8               | 43.7                | 16.08    |
| 8     | 10 (6)                 | 100              | 81.6               | 53.7                | 43.82    |
| 9     | 10 (2)                 | 80               | 47.3               | 56.2                | 26.58    |
| 10    | 10 (4)                 | 80               | 59.7               | 63.7                | 38.03    |
| 11    | 10 (10)                | 80               | 83.1               | 57.0                | 47.37    |

Note: [a] Reactions were carried out at 80 °C in 1,2-dichloroethane (5 mL) with soybean oil (10 g), TBHP (5.0 mmol), and the ZPS–PVPA–SO3H catalyst (10 mol%(wt%)); [b] conversions and selectivity were determined by GB/T1676-008 and GB/T 1677-2008 method.

In order to determine the optimal amount of ZPS–PVPA–SO3H, the reaction was firstly carried out in the presence of different amounts (1–20 wt%, based on soybean oil) at 80 °C in 1,2-dichloroethane...
using TBHP as an oxidant. The results showed that the conversions were increased from 32.1 to 81.3% with an increase in yield from 16.27 to 60.06% when the amount of catalyst was increased from 1 to 20 wt%. Moreover, an additional increase in the amount of catalyst did not show any positive effect on the conversion and selectivity of the soybean oil epoxide (Table 2, entry 5). Blank experiment showed that the ZPS–PVPA–SO$_3$H alone is inactive towards epoxidation of soybean oil, and a yield of only 0.34% was achieved (Table 2, entry 6). In addition, we screened the effects of different temperatures on the epoxidation of soybean oil. The results show that the conversion and selectivity increases with increasing temperature but the selectivity decreases when the temperature increases above 80 °C. A similar trend was found for the effect of reaction time on catalytic reactions. This is mainly attributed to the slow decomposition of TBHP, making formation of a by-product more likely at higher temperatures and over longer durations. Therefore, 80 °C and 6 h were chosen as the reaction time and temperature of the system.

2.7. Reusability of the ZPS–PVPA–SO$_3$H

To assess the recyclability of the ZPS–PVPA–SO$_3$H, the reaction system was separated by centrifugation after the reaction is completed, the catalyst was left untreated, and the reaction was continuously reacted according to the initial ratio. As shown in Table 3, it is obvious that the catalyst worked well for up to five cycles with no considerable decrease in reactivity (yield% from 60.06 to 55.25%). An unexpected discovery was that the catalytic activity of the catalyst was gradually restored at the 8th to 10th cycles of the catalyst when the ZPS–PVPA–SO$_3$H was allowed to stand in 2 mol/L of dilute hydrochloric acid overnight after the 7th reuse; similar results have been reported in the asymmetric epoxidation of olefin catalyzed by ZPS–PVPA–SalenMn [12]. This novel phenomenon is probably due to the nano-layered self-supporting function [21] of the inorganic zirconium phosphate portion of the catalyst structure. The catalyst may have a certain “memory function” and can be roughly restored to the original morphology in acid medium. However, the specific reasons remain to be further studied.

Table 3. The recycling of ZPS–PVPA–SO$_3$H in epoxidation of soybean oil.[a]

| Run | Conversion (%) | Selectivity (%) | Yield (%) |
|-----|----------------|-----------------|-----------|
| 1  | 78.2 (6)       | 76.8            | 60.06     |
| 2  | 77.9 (6)       | 75.4            | 58.74     |
| 3  | 77.1 (6)       | 74.2            | 57.21     |
| 4  | 76.8 (6)       | 73.8            | 56.68     |
| 5  | 76.0 (6)       | 72.7            | 55.25     |
| 6  | 70.1 (6)       | 66.3            | 46.48     |
| 7  | 61.3 (6)       | 50.9            | 31.20     |
| 8  | 76.3 (6)       | 69.4            | 52.95     |
| 9  | 75.8 (6)       | 67.8            | 51.39     |
| 10 | 70.6 (6)       | 62.9            | 44.41     |

Note: [a] Reactions were carried out at 80 °C in 1,2-dichloroethane (5 mL) with soybean oil (10 g), TBHP (5.0 mmol), and the ZPS–PVPA–SO$_3$H catalyst (10 mol%(wt%)); [b] conversions and selectivity were determined by GB/T1676-2008 and GB/T 1677-2008 method.

3. Material and Methods

3.1. Materials

Zirconyl chloride octahydrate, γ-propyl mercaptotrimethoxysilane (MPTMS), tert-butyl hydroperoxide (TBHP, 65%, wt%), and benzoyl peroxide (BPO) were supplied by Alfa Aesar (Tianjian, China). The 1-phenylvinyl phosphonic acid (PVPA) was prepared according to literature [22] and its structures were confirmed by $^1$H NMR, $^{31}$P NMR, and FT-IR. $^1$H NMR (CDCl$_3$):6.06 (d, 1H), 6.23 (d, 1H), 7.26–7.33 (m, 3H), 7.48 (m, 2H). $^{31}$P NMR (CD$_3$OD):15.9. IR (KBr):2710, 2240, 1500, 1200, 1040,
950, 780, 720, 700 cm\(^{-1}\). Other commercially available chemicals were laboratory-grade reagents from local suppliers. Soybean oil was purchased from a local supermarket ([I.N.] = 120).

3.2. Methods

XPS were recorded on ESCALab250 instrument (Thermo Fisher Scientific, USA). SEM were performed on SU8010 (JEOL, Japan) microscopy. EDS were performed on a JSM-7800F (JEOL, Japan) apparatus. TG-DSC analyses were performed on a SBTQ600 Thermal Analyzer (USA) with a heating rate of 20 °C·min\(^{-1}\) from 25 to 1000 °C under flowing N\(_2\) (100 mL·min\(^{-1}\)). The interlayer spacings were measured between 2.00 and 80.00° and X-ray tube settings of 40 kV and 5 mA.

3.3. Preparation of Catalysts

3.3.1. Synthesis of Zirconium poly(styrene-phenylvinyl-phosphonate)-phosphate (ZPS–PVPA)

The synthesis and characterization of ZPS–PVPA (Scheme 1) has been reported earlier by our group [22].

\[
\text{(ZPS-PVPA)}
\]

\[
\text{Zirconyl chloride octahydrate, } \quad \gamma\text{-propyl mercaptotrimethoxysilane (MPTMS), tert-butyl hydroperoxide (TBHP), and benzoyl peroxide (BPO) were supplied by Alfa Aesar (Tianjian, China). The 1-phenylvinyl phosphonic acid (PVPA) was prepared according to literature [22] and its structures were confirmed by 1H NMR, 31P NMR, and FT-IR. 1H NMR (CDCl}_3): 6.06 (d, 1H), 6.23 (d, 1H), 7.26–7.33 (m, 3H), 7.48 (m, 2H). 31P NMR (CD3OD): 15.9. IR (KBr): 2710, 2240, 1500, 1200, 1040, 950, 780, 720, 700 cm\(^{-1}\).}

\[
\text{Scheme 1. Synthesis of ZPS–PVPA.}
\]

3.3.2. Synthesis of Sulfonic Acid-Functionalized Zirconium Poly(styrene-phenylvinyl-phosphonate)-phosphate

ZPS–PVPA was functionalized by the condensation reaction between the –OH on the ZPS–PVPA surface and the –Si(OMe)\(_3\) groups of MPTMS [23]. Here, 0.50 g of (ZPS–PVPA) was swelled and ultrasounded in toluene (30 mL) for an hour. Subsequently, MPTMS (2 mL) was dropped into the suspension and then refluxed under vigorous stirring for 24 h in a N\(_2\) atmosphere. After the reaction, the mixture was filtered and the obtained solid was washed with toluene (30 mL × 3) to remove the residual MPTMS and dried at 60 °C overnight in a vacuum oven. The obtained product was abbreviated as ZPS–PVPA–SH. ZPS–PVPA–SO\(_3\)H was obtained as follows: a certain amount of H\(_2\)O\(_2\) (5.5 mL) was slowly added to the dispersion of ZPS–PVPA–SH (0.3 g) in 12.0 mL of methanol. The reaction was kept at room temperature for 24 h. The obtained solid was further treated with HCl (2.5 mL, 37 wt%) at ambient temperature for complete protonation [24]. The sample was separated by centrifugation and then washed with water and ethanol. After drying at 60 °C for 24 h in a vacuum oven, ZPS–PVPA–SO\(_3\)H was obtained (Scheme 2).
was determined through the GB/T1677-2008 method. The conversion and the yield to epoxide were calculated by the following equations:

\[ \text{Conversion} = \frac{[\text{I.N.}]_i - [\text{I.N.}]_f}{[\text{I.N.}]_i} \times 100 \]  

(1)

\[ \text{Selectivity} = \frac{[[\text{O.N.}]_i/\text{M.W(O)} \times 100] - [\text{I.N.}]_f/\text{M.W(I}_2\text{)} \times 100]}{[\text{I.N.}]_i} \times 100 \]  

(2)

\[ \text{Yield to epoxide} = \text{Conversion} \times \text{Selectivity} \times 100 \]  

(3)

where \( i \) and \( f \) represent, respectively, initial and final values, \( \text{M.W} \) is the molecular weight, \( \text{O.N.} \) is epoxy value, \( \text{I.N.} \) is iodine value, \( \text{M(O)} = 16 \), and \( \text{M(I}_2\text{)} = 254 \).

4. Conclusions

This paper provides a new solid acid catalyst for catalyzing epoxidized soybean oil. The catalytic results showed that the ZPS–PVPA–SO3H can efficiently promote the epoxidation of soybean oil. Furthermore, the ZPS–PVPA–SO3H could be easily separated from the products and recycled at least five times without significant loss of catalytic activity. Interestingly, the ZPS–PVPA–SO3H was kept in 2 mol/L of HCl overnight at the end of the 7th reaction, and the catalytic activity was gradually restored during the 8th to 10th cycles.

Author Contributions: X.C.Z. designed the experiments and wrote the paper. X.C.Z., X.Y.N., Z.W.T., Y.W., and C.W. performed the experiments. K.Y.S. analyzed the data and provided meaningful advice. X.Z. secured the funds.

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