Article

Synergistic Interactions between Ti–OOH and (PO$_4$[WO$_2$(O$_2$)]$_4$)$^{3-}$ of HPW/Zn-Ti Hydrotalcites: Efficient Heterogeneous Catalysts for the Epoxidation of Fatty Acid Methyl Ester

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A series of HPW/Zn-Ti layered double hydroxides (LDHs) were prepared by immobilizing phosphotungstic acid (HPW) on the Zn-Ti LDHs. Systematically characterizations were performed to elucidate their structure. These HPW/Zn-Ti LDHs hybrids were used as heterogeneous catalysts in the epoxidation of fatty acid methyl ester (FAMEs) with H$_2$O$_2$. The HPW/Zn-Ti LDHs showed higher activity than bulk HPW and Zn-Ti LDHs. The conversion of FAMEs and the selectivity to epoxy fatty acid methyl ester (EFAME) were up to 90.6 and 86.0%, respectively. (PO$_4$[WO$_2$(O$_2$)]$_4$)$^{3-}$ was presumed to be the active site for the epoxidation in this work. The formed oxygen-donating intermediate Ti–OOH transferred oxygen free radicals to (PO$_4$[WO$_2$(O$_2$)]$_4$)$^{3-}$ in the catalytic process, accelerating the transfer of oxygen free radicals. Therefore, high catalytic activity of HPW/Zn-Ti LDHs is related to the potential synergistic interactions of Ti–OOH and PW anions.

Keywords: Zn-Ti hydrotalcites, phosphotungstic acid intercalation, fatty acid methyl ester, epoxidation, synergistic interactions

Introduction

Epoxidized vegetable oils and products of their transformations, alkyl esters of fatty acids, have been widely used as solvents, lubricants, cosmetics, biofuel additives, stabilizers and plasticizers.[1-3] The utilization of epoxidized oils enables the polymers and composites to have mechanical, electrical, and thermal properties than their counterparts obtained from petrochemical products.[4] For instance, epoxidized fatty acid methyl esters (FAMEs) are good substitutes for phthalates that are banned in children's toys, medical supplies, food packaging and other plastic and rubber products in close contact with human body by the EU (European Union) and FDA (Food and Drug Administration). During the past decade, most of epoxidation processes in the industry have been conducted by indirect oxidation method, which produces excess acidic wastewater. Recently, solid catalysts such as metalloporphyrins,[5] methyl rhenium trioxide,[6] zeolites[7] and aluminum-based catalyst,[1,8] were employed for the epoxidation of FAMEs. However, these catalysts are disadvantageous in terms of high cost and difficulty in

preparation. From the perspective of green chemistry, we sought to prepare a novel catalyst with high conversion of FAMEs and excellent selectivity for epoxy fatty acid methyl ester (EFAME). Lin and Frei[9] confirmed that the active peroxide species formed upon interaction of H$_2$O$_2$ with solvent-free Ti silicalite molecular sieve in the reaction of H$_2$O$_2$-containing hydrocarbon oxidation. Heteropolyacids (HPAs), especially tungsten-containing HPAs, have attracted much attention for a long time as effective catalysts in the H$_2$O$_2$-based epoxidation of alkenes.[2,10,11] Although excellent activity was achieved by HPAs, there are numbers of drawbacks such as small specific surface area and the difficulty in recycle and reuse of the catalyst.

Recently, layered double hydroxides (LDHs), a class of anion clays consisting of brucite-like host layers and interlayer anions,[12] have received considerable attention because of their adjustable anionic exchange capacity, high metal dispersion, large surface area, as well as excellent thermostability.[13,14] The epoxidation of FAMEs is supposed to proceed via radical pathway. Therefore, the performance of HPAs as effective catalysts in the H$_2$O$_2$-based epoxidation of FAMEs can be enhanced by inserting HPAs into LDH, with the simultaneous immobilization of HPAs

for recycling. Recently, such research was focused to regulate the properties of hydrotalcites by modulating interlayer anions.[15,16] For instance, Li *et al.*[17] reported that phosphotungstic acid (HPW)/Mg-Al LDHs showed good performance in the epoxidation of FAMEs. Actually, the modulation of the electronic conductivity and redox of LDHs is dependent on the nature of cations in the layers.[18] In addition, both the experimental and theoretical results indicated that the introduction of Zn and Ti element into the hydrotalcite laminates can facilitate the absorption of photons and result in the transfer of electrons.[19] In view of this, HPW/Zn-Ti LDHs have a promising application in FAME epoxidation.

Herein, we devoted to investigate the epoxidation of FAMEs using di- and tetra-valent cationic metals containing LDHs (Zn and Ti). Zn-Ti LDHs with different Ti contents and hierarchical porous structures were synthesized by co-precipitation method and then PW anions were introduced into the interlayers through an ion-exchange process. The obtained catalysts led to a heterogeneous catalytic system for the epoxidation of FAMEs with H_2O_2, showing high conversion and selectivity. Further, the obtained catalysts exhibited excellent reusability.

Experimental

Materials

Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), titanium tetrachloride ($TiCl_4$) and urea ($CO(NH_2)_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemical reagents were of analytical grade and used without further purification.

Catalyst preparations

The Zn-Ti containing layered double hydroxides (Zn-Ti LDHs) were hydrothermally prepared. In a typical synthesis, 0.22 mL of $TiCl_4$, 1.79 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 3.0 g of urea were dissolved in 100 mL deionized water under vigorous stirring. The resulting mixture was aged in an autoclave at 130 °C for 48 h. After that, the solid was separated by centrifugation, washed thoroughly with deionized water, and finally dried overnight at 60 °C. The LDHs with different Zn^{2+}/Ti^{4+} molar ratios were prepared using the same procedure by varying the Ti^{4+} content and denoted as Zn-Ti-x LDHs (x = 2, 3, 4…, representing the Zn/Ti molar ratio). HPW/Zn-Ti-x LDHs were prepared by ion-exchange with an aqueous solution of phosphotungstic acid (HPW, 0.004 mol L⁻¹) at 90 °C. The mixture was ultrasonicated (900 W, 20 kHz) for 5 h under the protection

of nitrogen. The solid was separated by centrifugation, washed with water and then dried at 80 °C.

Catalyst characterization

X-ray diffraction (XRD) analysis was conducted on Bruker D8 Advance powder X-ray diffractometer, using Cu Kα₁ (λ = 1.542 Å) radiation source at 40 kV and 200 mA, from 5 to 80° with a scan rate of 20° min⁻¹. The surface area and pore volume were investigated by nitrogen sorption experiment on BELSORP-MAX. The contents of Zn, Ti, and W were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a PerkinElmer ICP-OES Optima 3000 instrument. X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis HSi photoelectron spectrometer at a pressure of about 3×10^{-9} Pa using Al Kα X-ray as the excitation source. The Fourier transform infrared (FTIR) spectra were obtained on Agilent Cary 660 in the range of 4000 to 400 cm⁻¹ on a KBr pellet. The morphology was observed by scanning electron microscopy (SEM) on a Hitachi S-4800 instrument.

Catalytic tests

In a typical experiment, the fatty acid methyl ester (10 g), methanol (16 mL) and as-synthesized LDHs were mixed in a 50 mL three-neck flask outfitted with a condenser and thermometer, followed by the slowly addition of H_2O_2 (mass fraction of 30%). The solution was stirred vigorously at 70 °C for 7 h. The iodine value of EFAME was determined according to ASTM D5554-15[20] and their epoxy value was determined according to ASTM D1652-11e1.[21] The conversion and selectivity were calculated by the following equations 1 and 2:

$$\text{Conversion} = (\text{raw material iodine value} - \text{epoxide product iodine value}) / \text{raw material iodine value} \times 100\% \qquad (1)$$

$$\text{Selectivity} = [\text{epoxide product epoxy value} \times M(I_2)] / [M(O) \times (\text{raw material iodine value} - \text{epoxide product iodine value})] \times 100\% \qquad (2)$$

where $M(I_2) = 254$ and $M(O) = 16$, corresponding to the relative atomic mass of I_2 and O, respectively.

Five-run recycling tests were used to assess the reusability of HPW/Zn-Ti-3 LDHs. After reaction, the catalyst was separated from the reaction mixture by centrifugation, washed by anhydrous ethanol, and reused in the next run.

Results and Discussion

Catalytic characterization

Figure 1a shows XRD patterns of Zn-Ti LDHs. The reflections of (003), (006), (009), (100), (101), (012), (110) and (113) were observable and they are in line with the typical LDH materials.[22] Several weak diffraction peaks at the 2θ of 22, 31 and 36° can attributed to the zinc hydroxide impurity (JCPDS No. 20-1437). The XRD pattern of HPW/Zn-Ti-3 LDHs shows the diffraction peaks in the ranges of 15-20° and 25-40° corresponding to the Keggin structure of polyoxometalates (POMs). Moreover, the peaks at (003), (006), (009) slightly shift to the lower scattering angle compared to the ones in the XRD pattern of Zn-Ti-3 LDHs. According to the Bragg equation of 2d sinθ = nλ, the corresponding interlayer spacing of HPW/Zn-Ti-3 LDHs was calculated to be 0.88 nm, larger than one of Zn-Ti-3 LDHs (0.76 nm). Such increase of interlayer spacing should come from the intercalation of bulky PW anions with much larger volume into the interlayer space of Zn-Ti-3 LDHs.[23] SEM images of the as-prepared Zn-Ti-3 LDHs and HPW/Zn-Ti-3 LDHs are presented in Figures 1b and 1c. These two materials exhibit microspheric morphology with a diameter of about 5-10 μm. The lamellae of HPW/Zn-Ti-3 LDHs are larger than the ones of Zn-Ti-3 LDHs and demonstrate a more uniform distribution.

Table 1 summarizes the chemical composition and textural properties of the prepared catalysts. The elemental analysis results show that they possess the Zn/Ti molar ratios close to the nominal one, suggesting that both Zn and Ti cations were approximately precipitated under the present precipitation conditions. The recovered HPW/Zn-Ti-3 LDHs sample after reaction kept almost the same content of PW anions as the fresh one, suggesting that these PW anions were stable because they were mainly bonded to the laminates through the Coulomb force. The Brunauer-Emmett-Teller (BET) surface areas slightly decrease with higher Zn/Ti molar ratios and the reason can be assigned to the replacement of Ti by Zn with a larger ion radius.[24] HPW/Zn-Ti-3 LDHs exhibited higher specific surface area (154 $m^2 g^{-1}$) and pore volume (0.1922 $cm^3 g^{-1}$) than others. This phenomenon may be attributed to the intercalation of PW anions and the exfoliation of LDH lamella during the ion-exchange process.[25]

Figure 2a illustrates the FTIR spectra of the as-synthesized LDHs in the region of 500-4000 cm^{-1}. The strong and broad band observed at 3400 cm^{-1} corresponds to the O–H stretching vibration of surface and interlayer water molecules. The peak at 1640 cm^{-1} is assigned to deformation
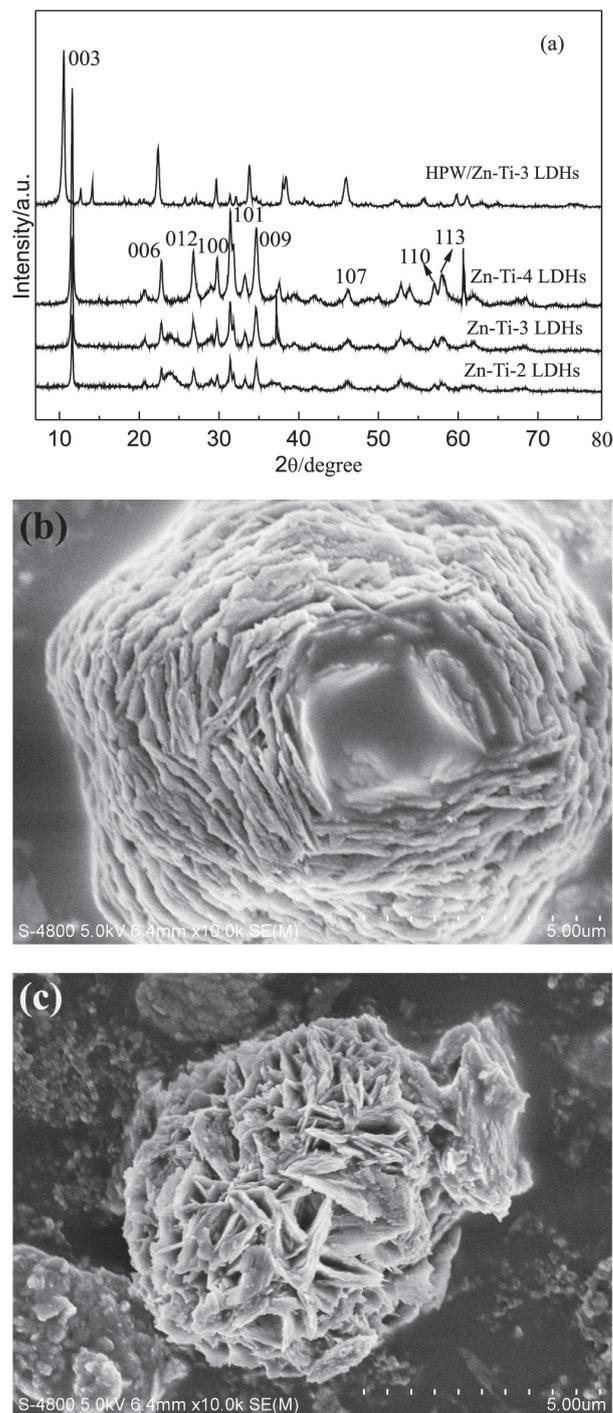
Figure 1. (a) XRD patterns of different LDHs; SEM images of (b) Zn-Ti-3 LDHs and (c) HPW/Zn-Ti-3 LDHs.

bending vibration of interlayer water molecules. Intense bands at around 1422 cm^{-1} are attributable to the symmetric stretching vibrations of the interlayer CO_3^{2-}, indicating that the synthesized LDHs have absorption peak of hydrotalcite. The characteristic absorption peaks of PW anions appear at 950 cm^{-1} (W−O−W) and 880 cm^{-1} (W=O), reflecting the partial replacement of interformational CO_3^{2-} with PW anions.[26] XPS spectra (Figure 2b) indicate that the

Table 1. Chemical composition and textural properties of the catalysts

Sample	Mole ratios (Zn/Ti/W)		S_{BET}^{a} / (m² g⁻¹)	V_p^{b} / (cm³ g⁻¹)
	Theoretical	Experimental		
Zn-Ti-2 LDHs	2:1	2.121:1	134	0.1790
Zn-Ti-3 LDHs	3:1	2.893:1	129	0.1808
Zn-Ti-4 LDHs	4:1	3.822:1	122	0.1800
HPW/Zn-Ti-3 LDHs	3:1:0.1	3.132:1:0.110	154	0.1922
Recovered HPW/Zn-Ti-3 LDHs	3:1:0.1	3.120:1:0.108	148	0.1895

[a]Brunauer-Emmett-Teller (BET) surface area; [b]total pore volume.

surface is essentially dominated by Ti⁴⁺. Ti $2p_{1/2}$ and $2p_{2/3}$ spin-orbital splitting of Zn-Ti-3 LDHs are located at the binding energies of 463.6 and 458.0 eV, respectively. The peak separation of 5.6 eV between the Ti $2p_{1/2}$ and $2p_{2/3}$ signals is in good agreement with the reported value.[27] The Ti $2p_{1/2}$ and Ti $2p_{2/3}$ spin-orbital splitting of HPW/Zn-Ti-3 LDHs are located at the binding energies of 464.2 and 458.4 eV, the positive displacement of that are 0.6 and 0.4 eV, respectively. This phenomenon is attributed to the substitution of CO_3^{2-} by PW anions, and that causes

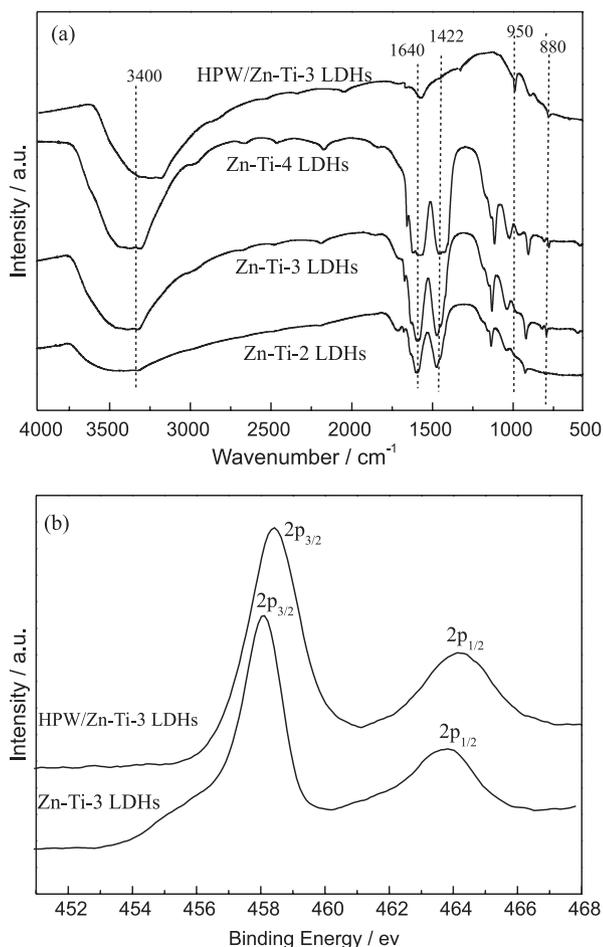strong interaction with the Ti cations and subsequently affect the electron state of Ti cations.

Catalytic performances

The Zn-Ti LDHs modified with PW anions were used as heterogeneous catalysts in the epoxidation of FAMEs with H_2O_2. Taking into account the important role of Ti in the epoxidation, the influence of Zn/Ti molar ratio was investigated in the reaction, as shown in Table 2. HPW/Zn-Ti-x LDHs can efficiently catalyze the epoxidation of FAMEs with high conversion and selectivity to the target products. Both the conversion and selectivity are much superior to the ones catalyzed by Zn-Ti-x LDHs, suggesting that the PW anions are the active sites. Among the three HPW/Zn-Ti-x LDHs catalysts, HPW/Zn-Ti-3 LDHs give the highest conversion of 90.6% and selectivity of 86.0%, reflecting the significant influence of the Ti content on the reaction. This is further reflected by the weak activity of HPW/Zn-Al-3 LDHs. The comparisons indicate the improvement of Ti⁴⁺ in the epoxidation reaction, which may be attributable to the synergistic effect of PW anions and

Figure 2. (a) FTIR spectra of catalysts; (b) XPS spectra of the Ti 2p line.

Table 2. The conversion and selectivity in the epoxidation of FAMEs with H_2O_2

No.	Catalyst	Conversion / %	Selectivity / %
1	HPW/Zn-Ti-2 LDHs	85.4	82.2
2	HPW/Zn-Ti-3 LDHs	90.6	86.0
3	HPW/Zn-Ti-4 LDHs	87.1	79.5
4	HPW/Zn-Al-3 LDHs	63.4	20.2
5	Zn-Ti-2 LDHs	52.2	8.1
6	Zn-Ti-3 LDHs	55.1	9.2
7	Zn-Ti-4 LDHs	56.3	8.4
8	$Zn(OH)_2$	4.8	16.5
9	$Ti(OH)_4$	2.9	23.4
10	$Na_3[PW_{12}O_{40}]$	17.8	8.2

Reaction temperature: 70 °C; reaction time: 7 h; $n(H_2O_2)/n$(double bond), 1.5:1; m(catalyst)/m(reactants), 0.07:1.

adequate Ti^{4+}.[28] Impurities such as $Zn(OH)_2$ and $Ti(OH)_4$ may co-exist in the catalysts and exhibit low conversion and selectivity, suggesting their weak contribution to the activity. $Na_3[PW_{12}O_{40}]$ was also inactive in the reaction, demonstrating that the immobilization of PW anions on the support of hydrotalcite played a key role in epoxidation reaction.

The influence of various reaction conditions was investigated in the HPW/Zn-Ti-3 LDHs catalyzed epoxidation of FAMEs. Figure 3a shows the influence of the catalyst dosage. Suitable catalyst dosage can match the rate of H_2O_2 decomposition, the rate of double bond activation and epoxidation.[29] The FAMEs conversion is found to increase gradually with the increasing amount of catalyst from 3 to 5% m/m, due to the increased active sites. The same pattern was observed in selectivity to EFAME. The reason is that low amount of catalyst leads a sufficient reaction while excess catalyst will accelerate the side effects. It could be concluded that 7.0% catalysts dosage was optimum in the present catalytic system. The reaction time is also an important factor for the catalytic performance of the catalyst, as seen in Figure 3b. The conversion was low

in the first four hours, due to the initiation of free radicals in this region. Then, the conversion increases rapidly with the reaction time and reaches the maximum at 7 h. Therefore, the optimum reaction time is 7 h.

The amount of H_2O_2 was investigated subsequently as shown in Figure 3c, indicating that the optimum molar ratio of H_2O_2 to double bond ($n(H_2O_2)/n$(double bond)) is 1.5:1. At the beginning, the conversion and selectivity increase along with the increase of H_2O_2, and then reach the maximum value at $n(H_2O_2)/n$(double bond), 1.5:1. Excess H_2O_2 leads to a significant decrease of the selectivity and to a slight increased conversion. The increased H_2O_2 is favorable for the epoxidation reaction, but the existence of water will promote the ring-opening reaction on Lewis acidic centers (such as Ti^{4+}) and thus decrease the selectivity to EFAME. The influence of reaction temperature is illustrated in Figure 3d. FAMEs conversion increases continuously with the elevation of the reaction temperature from 55 to 70 °C, affording an optical reaction temperature of 70 °C. This could be attributed to enhance accessibility of the reactant molecules to the active sites in a multiphase catalytic system.[30] The selectivity of EFAME is found to
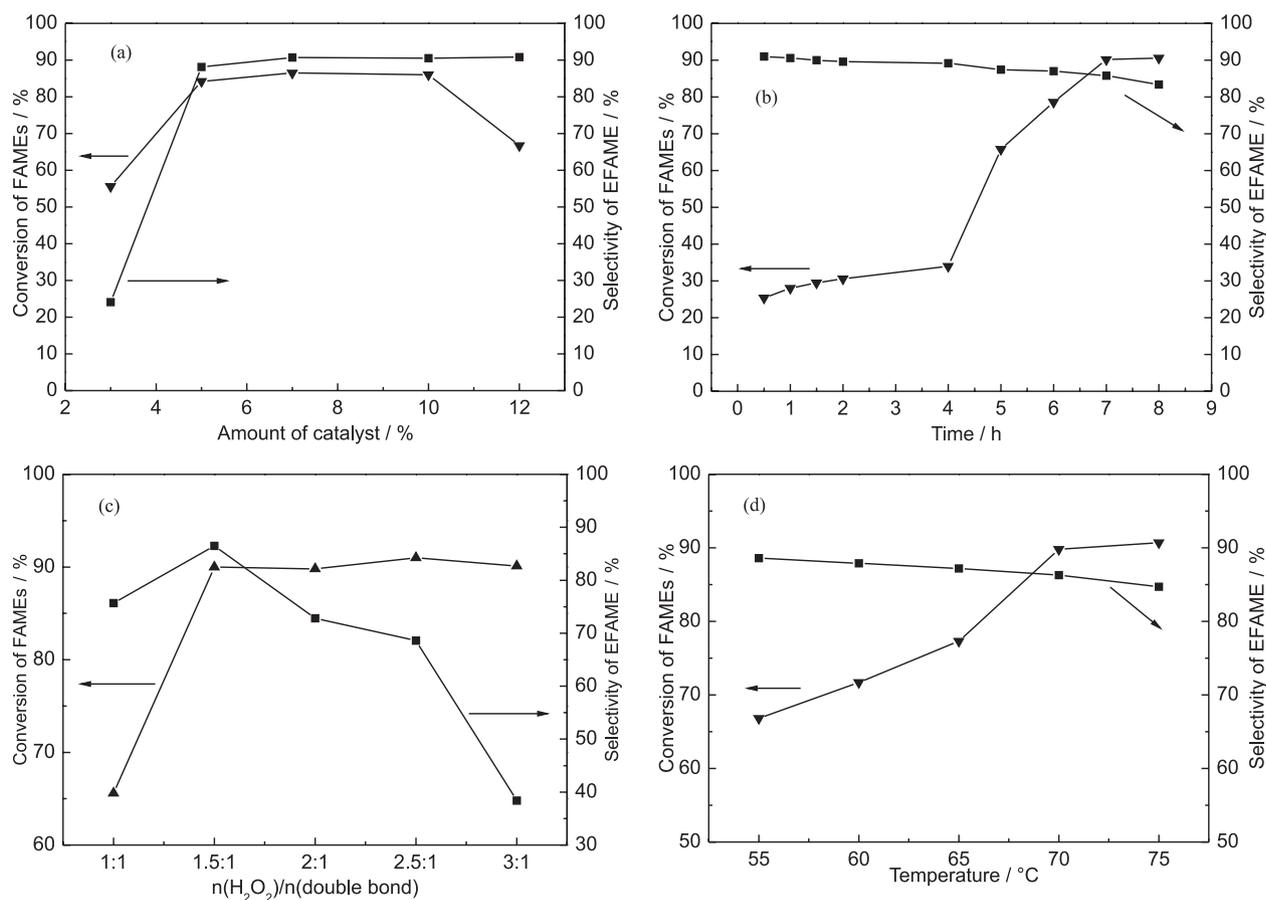

Figure 3. Activity of HPW/Zn-Ti-3 LDHs in the epoxidation of FAMEs under different reaction conditions: (a) 70 °C, 7 h, $n(H_2O_2)/n$(double bond), 1.5:1; (b) 70 °C, $n(H_2O_2)/n$(double bond), 1.5:1, m(catalysts)/m(reactants), 0.07:1; (c) 70 °C, 7 h, m(catalysts)/m(reactants), 0.07:1; (d) 7 h, $n(H_2O_2)/n$(double bond), 1.5:1; m(catalysts)/m(reactants), 0.07:1.

decrease with the temperature increase, indicating that a high temperature is more likely to cause ring-opening reaction. The reaction is triphasic system with aqueous, organic and solid phases, where the mass transfer is a critical factor. Based on this consideration, the rotational speed was investigated (Figure S1, Supplementary Information). The result indicates that the rotational speed only slightly affects the conversion and selectivity, revealing the neglecting of the mass transfer in this reaction.

The reusability of HPW/Zn-Ti-3 LDHs was evaluated in five-run recycling tests. As shown in Figure 4a, the catalyst can be easily recovered and reused without apparent deactivation for at least three cycles. In the 5th run, still high conversion of 81.4% and selectivity of 84.9% was achieved, reflecting the well reusability. The FTIR characterizations of the recovered catalyst in Figure 5 demonstrate the well preserved structure after reaction. The absorption peak at 950 cm^{-1} for the W–O–W bond becomes weakened, while the absorption peak near 880 cm^{-1} for the W=O bond is relatively enhanced. Such variation is attributable to the transformation of the original Keggin type PW anions into $(PO_4[WO(O_2)_2]_4)^{3-}$ species and the activation by CH_3OH and H_2O_2 to form $(PO_4[WO_2(O_2)]_4)^{3-}$ moieties in the subsequent catalytic epoxidation process. Leaching of PW anions was monitored by measuring the P and Ti concentration in the reaction solution after each run. The result in Figure 4a indicates that the leaching mainly occurred during the 1st and 2nd run, which comes from the existence of certain unstable Ti and PW anions formed during the catalyst preparation and responds to the deactivation during the recycling test. Nonetheless, leaching becomes negligible with recycling, reflecting that the catalyst tends to be stable.

The titanium complex and H_2O_2 can produce an oxygen-donating intermediate (Ti−OOH) in the epoxidation reaction, which makes the peroxidic oxygen more electrophilic and labile to attack.[31] The investigation of Keggin-type PW anions in the epoxidation reaction indicated that $[PW_{12}O_{40}]^{3-}$ could form smaller active species $(PO_4[WO_2(O_2)]_4)^{3-}$, $(PO_4[WO(O_2)_2]_4)^{3-}$ in the presence of H_2O_2.[32,33] Based on these results, the most possible reaction mechanism for the HPW/Zn-Ti-3 LDHs catalyzed epoxidation can be described as Figure 4b. The catalytic cycle starts from the reaction of H_2O_2 with Ti–OH to form negative charge surplus peroxide hydroxy intermediates Ti–OOH, providing excess oxygen free radicals. Simultaneously, $[PW_{12}O_{40}]^{3-}$ hydrolysis occurs in the presence of water and methanol. Due to the strong electrostatic interaction of Ti–OOH and $[PW_{12}O_{40}]^{3-}$, $(PO_4[WO_2(O_2)]_4)^{3-}$ gets four oxygen free radicals provided
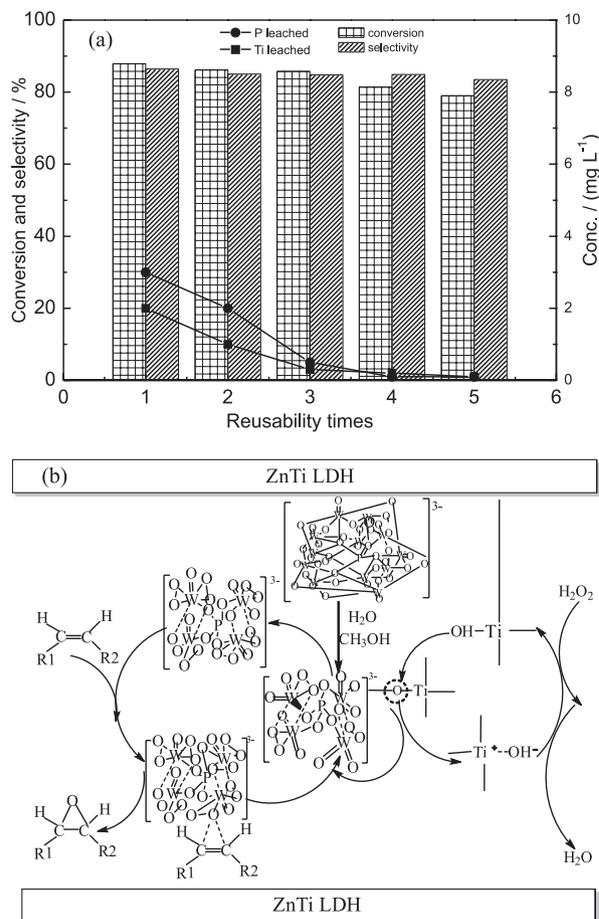
Figure 4. (a) Reusability of HPW/Zn-Ti-3 LDHs and the leached of P and Ti; (b) proposed reaction mechanism. Reaction conditions: 70 °C, 7 h, $n(H_2O_2)/n$(double bond), 1.5:1; m(catalyst)/m(reactants), 0.07:1.
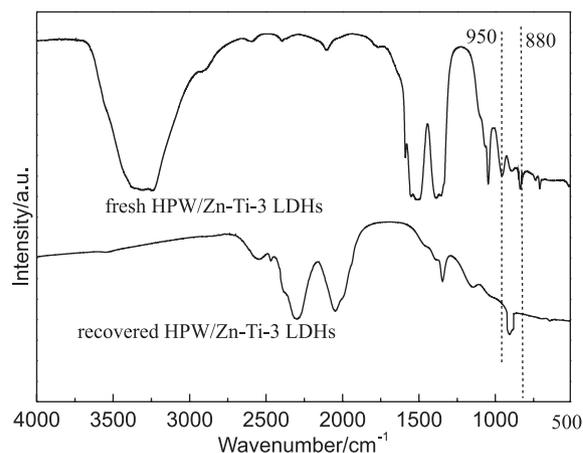
Figure 5. FTIR spectra of fresh and recovered catalysts.

by Ti–OOH and changes into $(PO_4[WO(O_2)_2]_4)^{3-}$ that is supposed to be the active site for epoxidation. Finally, the $(PO_4[WO(O_2)_2]_4)^{3-}$ is resumed to its original state of $(PO_4[WO_2(O_2)]_4)^{3-}$ by transferring its oxygen to the double bond of fatty acid methyl ester to produce the corresponding epoxy fatty acid methyl ester.

Conclusions

A series of Zn-Ti LDHs with lamellar structures were synthesized by co-precipitation method and served as the supports of PW anions, affording the catalyst HPW/Zn-Ti LDHs by inserting phosphotungstic acid into the Zn-Ti LDHs interlayer in an ion-exchange process. The resulting HPW/Zn-Ti-3 LDHs exhibited enhanced catalytic activity in the epoxidation of FAMEs with H_2O_2. Remarkable epoxidation activity may be ascribed to the synergetic catalysis between Ti–OOH and $(PO_4[WO_2(O_2)]_4)^{3-}$ that promoted the transfer of oxygen free radicals. The highest FAMEs conversion reached 90.6% with 86% of the selectivity to EFAME, when the reaction was carried out at 7 h at 70 °C with $n(H_2O_2)/n$(double bond) 1.5:1 and m(catalysts)/m(FAMEs) 7.0%. Moreover, HPW/Zn-Ti-3 LDHs still retain a high activity after 5 recycles in the epoxidation reaction.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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