Research Article

Hydrophilic Ti-MWW for catalyzing epoxidation of allyl alcohol

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Abstract

Titanosilicates are widely applied in the alkene epoxidation reactions with high reaction rate and selectivity to desired products. Their catalytic performance depends on the structure topology, the micro-environment of Ti active sites, and the hydrophobicity/hydrophilicity of zeolite framework. Herein, we focus on a hydrophilic substrate of allyl alcohol (AAL) and investigated catalytic performance of four titanosilicates (TS-1, Ti-MOR, Ti-MWW, and Re-Ti-MWW) in the AAL epoxidation reaction with hydrogen peroxide as the oxidant. Among them, Re-Ti-MWW, synthesized via the post-modification of Ti-MWW with piperidine, exhibited the highest activity. Moreover, the preferred solvent changed from MeCN for Ti-MWW to H_2O for Re-Ti-MWW. The relative diffusion rate of AAL over Re-Ti-MWW was up to 466×10^{-7} s^{-1}, much larger than those of other zeolites. The higher diffusion rate of Re-Ti-MWW was probably derived from the higher framework hydrophilicity as revealed by the smaller water contact angle of Re-Ti-MWW compared to the other zeolites, which contributed to the high activity in AAL epoxidation. In the continuous slurry reactor, Re-Ti-MWW achieved a high catalytic lifetime of 163 h, with the selectivity of desirable glycidol product maintained at > 97% in the H_2O solvent system, showing high potential as an industrial catalyst for the AAL epoxidation reaction.

Keywords: Titanosilicates, Ti-MWW zeolite, allyl alcohol epoxidation, hydrophilic, diffusion rate

INTRODUCTION

Glycidol (GLY) is an important oxygenated derivative of allyl alcohol (AAL), which is mainly used as a stabilizer in natural oils, emulsion breakers, and dye delamination agents. Generally, GLY is produced by the chloropropane method or the epoxidation of AAL. However, the chloropropane method leads to the generation of chlorine waste, causing serious environmental problems, while the epoxidation method using V_2O_5, Cr_2O_3, and WO_3 as catalysts has problems in regeneration and reusability[1-5]. Therefore, developing highly active and reusable catalyst to construct a green process for GLY production is desirable.

Zeolite, as a kind of representative solid acid catalyst, is widely used in the petrochemical industry[6]. The framework Si or Al can be partially replaced by the transition metals, such as Ti and Sn, to fabricate heteroatom-containing zeolites, which exhibit high activity in selective oxidation reactions[7-10]. TS-1 zeolite, with Ti isomorphously incorporated into MFI structure, is the first-generation titanosilicate and has been used in several industrial reactions using H_2O_2 as the oxidant, such as cyclohexanone ammoximation and propene epoxidation reactions[11-13]. However, the medium-size 10-membered ring (MR) pores of TS-1 suffer diffusion restrictions when processing large-size substrates[14]. Afterward, Ti-MWW with 12MR large cavities and surface half cups was developed. Ti-MWW exhibits higher conversion than TS-1 in the propylene and cyclohexene epoxidation[15]. The catalytic activity of Ti-MWW in olefin epoxidation reactions can be further enhanced by post-modifications, such as fluoride treatment or piperidine (PI)-assisted 3D to 2D structural transformation[16-20].

For the titanosilicate/H_2O_2 catalytic system, the pore size of titanosilicate affects the mass transfer of guest molecules (both reactants and products), while the framework hydrophobicity affects the diffusion rate and enrichment ability of substrate molecules (including organic substrates and H_2O_2)[8]. Na *et al.* converted surface Si-OH groups in layered TS-1 zeolite into Si-F groups through the NH_4F treatment, which effectively improved the epoxidation activity in 1-hexene epoxidation reaction because of the enhancement of framework hydrophobicity[20]. Wang *et al.* increased the hydrophilicity of TS-1 to enrich H_2O_2 around Ti sites, resulting in higher catalytic activity by improving the H_2O_2 activation rate[21]. Bregante *et al.* reported that the large number of Si-OH groups in Ti-Beta near the Ti active centers disrupted the transition state of epoxidation reaction by hydrogen bonding with H_2O molecular clusters, generating an entropy increase for the reaction. The highly hydrophilic Ti-Beta gave an epoxidation turnover rate that was 100 times larger than that of hydrophobic Ti-Beta in the 1-hexene epoxidation reaction[22-25].

In addition to the intrinsic Ti activity and the confinement environment from zeolitic structural properties, the solvent effect is also a factor worthy of attention. Solvents can facilitate mass and heat transfer, and more importantly, the protic solvents can participate in the construction of the 5-MR intermediate with Ti-OOH active species. To form Ti-OOH active species, the H_2O_2 molecules need to undergo hydrogen proton transfer[26,27]. Bonino *et al.* proposed that protic solvent molecules (H_2O or MeOH) could act as hydrogen proton carriers to facilitate the formation of Ti-OOH by forming hydrogen bonding networks with H_2O_2 and Ti-OH in the reaction system[28]. Theoretical calculations by Wang *et al.* revealed that the non-protic solvent MeCN has no effect on the reaction path and kinetics, while the protic solvent MeOH can co-adsorb with H_2O_2 on Ti active sites through hydrogen bonding to reduce the dissociation energy of H_2O_2 and promote the hydrogen proton transfer[29]. Wang *et al.* revealed that the smaller the molecular size of a protic solvent, the less effect of the formed 5MR intermediate on the diffusion of the substrate[30]. Thus, water is the preferred solvent once it matches the reaction system of alkene epoxidation. On the one hand, it is a small-size molecule, imposing fewer diffusion constraints. On the other hand, H_2O does not cause environmental pollution as a solvent[31,32].

In previous reports, several titanosilicates were evaluated in the catalytic epoxidation of AAL; among them, Ti-MWW showed high GLY yields[1]. To construct a more efficient catalytic system for AAL epoxidation reaction, a modified Ti-MWW catalyst, obtained by PI-assisted structural rearrangement, was used as a catalyst in the present study, and its epoxidation activity was compared with Ti-MWW, TS-1, and Ti-MOR. Re-Ti-MWW exhibited the highest turnover rate and GLY selectivity among all the four catalysts. After the PI-assisted structure rearrangement, some of the tetrahedrally coordinated Ti species were transformed into hexa-coordinated ones with higher activity by interacting with PI molecules. The 3D to 2D structural transformation increased the amount of surface Si-OH groups, thus increasing framework hydrophilicity and altering the solvent effect for the AAL epoxidation reaction. Despite having the same layer structure as Ti-MWW, the preferred solvent changed from MeCN for Ti-MWW to the greener water for Re-Ti-MWW in the AAL epoxidation reaction. The reaction kinetics of AAL epoxidation over Ti-MWW and Re-Ti-MWW were compared to reveal the intrinsic reason for activity enhancement. Finally, the catalytic performance of Re-Ti-MWW was evaluated in the continuous AAL epoxidation using H_2O as the solvent, giving a long lifetime of 163 h with the addition of $(NH_4)_2CO_3$.

EXPERIMENTAL

Synthesis of different titanosilicates

Ti-MWW zeolites were hydrothermally synthesized as described previously[33], with a molar composition of 1.0 SiO_2 : 0.03 TiO_2 : 1.4 PI : 0.67 B_2O_3 : 19 H_2O, where boric acid was used as the crystallization agent and PI as the structure-directing agent. The Si and Ti sources were silica sol solution (30 wt%) and tetrabutyl orthotitanate (TBOT), respectively. The synthetic gel was heated at 443 K for 7 days under dynamic conditions. The product was collected by filtration, washing with distilled water, and drying at 373 K for 12 h. Then, an acid treatment by 2.0 M HNO_3 aqueous solution was performed with a solid-to-liquid weight ratio of 1:50 at 413 K for 12 h to remove extra-framework Ti, followed by calcination at 823 K for 6 h. For comparison, TS-1 zeolites were prepared following a reported protocol[18]. Ti-MOR zeolites were obtained by commercial H-MOR combining dealumination and $TiCl_4$ treatment, according to the previous work[34,35].

PI-assisted post-treatment of Ti-MWW

Re-Ti-MWW zeolites were prepared as described previously[16]. Subsequently, 2.84 g of PI was added to 22.5 g of water. After being stirred for 5 min, 5 g of Ti-MWW zeolite was added. The obtained gel was stirred for 1 h, then transferred to a Teflon vessel and hydrothermally treated at 443 K for 24 h. Finally, the solid product was filtered, washed with deionized water, and dried at 353 K for 12 h. The solid product was denoted as Re-Ti-MWW. It should be noted that the PI molecules were occluded in the layered MWW structure in the following characterization and catalytic reactions.

Materials characterization

The crystalline structures of zeolites were confirmed using an Ultima IV X-ray powder diffractometer (XRD) from Rigaku, with a Ni-filtered CuKα X-ray source (λ = 1.5406 Å), and the voltage and current were 35 kV and 25 mA, respectively. The content of organic species and water in catalysts was determined by a TGA/SDTA 851 thermogravimetric (TG) analyzer from Mettler Toledo. The sample was heated from 303 to 1,073 K in air. The solid-state NMR spectra of catalysts were measured using a VNMRS-400 MB NMR spectrometer manufactured by VARIAN[13]. C MAS NMR spectra were determined using adamantane as a standard at 100.54 MHz and 5 kHz[29]. Si MAS NMR spectra were determined using $[(CH_3)_3SiO]_8SiO_{12}$ as a standard at 79.43 and 3 kHz. Scanning electron microscope (SEM) images were obtained from a Hitachi S-4800 microscope with a test voltage of 3 kV. The coordination state of titanium species was characterized by a ultraviolet-visible (UV-vis) spectrophotometer from Shimadzu, using $BaSO_4$ powder as the reference sample. H_2O and N_2 physisorption measurements were tested using BELSORP instrument at 298 and 77 K, respectively. Prior to physisorption, the catalysts without organic species were activated under vacuum at

573 K for 6 h, while those containing organic species were treated under vacuum at 423 K for 12 h. The surficial wettability of the samples was characterized on a water contact angle (WCA) tester (USA Kino Industry Co., Ltd, USA) via the sessile drop method. The sample was first pelletized and then placed on the test platform. The WCA values were recorded at three different points on the sample, with the average value reported. Inductively coupled plasma atomic emission spectrometry (ICP-AES) collected on an IRIS Intrepid II type XSP was used to determine the content of various elements in the catalysts. Before the measurements, all samples were digested with 40 wt% HF solution and diluted with deionized water.

Diffusivity measurement

The diffusivity of AAL over various titanosilicates was determined by gravimetric analysis using a TG analyzer. The catalyst was pre-treated at 423 K under nitrogen for 2 h and then cooled down to 313 K to keep the weight baseline stable. Subsequently, AAL was brought into the TG by nitrogen gas (50 mL·min^{-1}) at 313 K for 2 h. Fick's second law was used to calculate the effective diffusion coefficient. At the beginning of the adsorption, the formula can be well approximated as follows:

$$\frac{Q_t}{Q_\infty} = \frac{6}{\sqrt{\pi}}\left(\frac{D}{r^2}\right)^{1/2} t^{1/2}$$

Q_t: the normalized hydrocarbon uptake; D: the diffusivity; r: effective diffusion length; t: time.

Catalytic performance

Batchwise allyl alcohol epoxidation

The AAL epoxidation was performed in a 35 mL quartz reaction tube. In a typical experiment, 30 mg catalyst, 30 mmol H_2O_2 (30 wt% aqueous solution), 30 mmol AAL, and 5 mL solvent were added into the reaction tube. The reaction solution was stirred at 313 K for 0.5 h. After reaction, the catalyst was separated by centrifugation. Cyclopentanone was added as the internal standard, and the liquid-phase product was analyzed by gas chromatography (Shimadzu 2014, FID detector) equipped with a Rtx-Wax capillary column. The residual H_2O_2 was titrated with 0.05 M $Ce(SO_4)_2$ aqueous solution.

Glycidol hydrolysis reaction

The GLY hydrolysis reaction was performed in a 35 mL quartz reaction tube. Following that, 10 mmol GLY, 5 mL solvent, 10 mmol H_2O_2 (30 wt% aqueous solution), and 100 mg catalyst were introduced into the reaction tube and stirred at 313 K for 20-300 min. After reaction, the catalyst was separated by centrifugation, and the remaining reaction solution was analyzed by gas chromatography.

Continuous liquid-phase allyl alcohol epoxidation

The continuous epoxidation reaction of AAL was performed in a slurry bed reactor. The reaction temperature was controlled by a water bath [Supplementary Scheme 1]. The AAL/H_2O_2/H_2O solution was fed via a peristaltic pump to the reactor, where 1 g of catalyst and 35 mL of water were added in advance at 40 °C. The gauze was used as a filter for solid-liquid separation, and the liquid product was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Characterization of different zeolites

The XRD patterns revealed that Ti-MWW, TS-1, and Ti-MOR exhibited high crystallinity without impurity, characteristic of the typical MWW, MFI, and MOR structures, respectively [Figure 1A]. Re-Ti-MWW
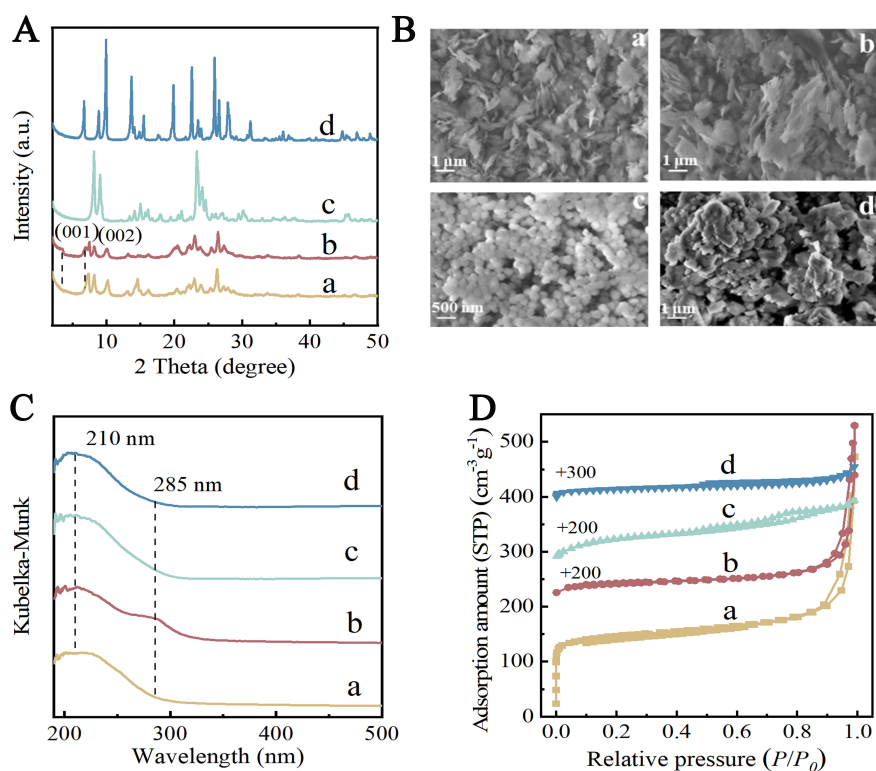
Figure 1. (A) XRD patterns; (B) SEM images; (C) UV-vis spectra; and (D) N_2 adsorption-desorption isotherms at 77 K of (a) Ti-MWW, (b) Re-Ti-MWW, (c) TS-1, and (d) Ti-MOR. XRD: X-ray powder diffractometer; SEM: scanning electron microscope; UV-vis: ultraviolet-visible.

showed a similar XRD pattern as that of Ti-MWW, except for the differences in the low-angle region. Two characteristic diffraction peaks at $2\theta = 3.5°$ and $6.7°$ attributed to the (001) and (002) crystal planes of layered MWW structure, respectively, appeared in the XRD pattern of Re-Ti-MWW due to the structural change from 3D Ti-MWW to 2D layered Re-Ti-MWW with the assistance of PI [Scheme 1]. The interlayer Si-O-Si linkages were broken in this process, allowing the PI molecules to be inserted between the MWW layers[15]. The presence of PI molecules in Re-Ti-MWW was further confirmed by the TG analysis and[13] C MAS NMR spectrum [Supplementary Figure 1]. Ti-MWW and Re-Ti-MWW had similar nanosheet morphology with a thickness of ~50 nm [Figure 1B (a) and (b)]. TS-1 showed nanoparticle morphology with a diameter of ~ 100 nm [Figure 1B (c)], while Ti-MOR showed irregular crystals on the micrometer scale [Figure 1B (d)]. All the four titanosilicates showed distinct absorption peaks at 210-220 nm attributed to tetrahedrally coordinated Ti species in UV-vis spectra [Figure 1C]. A shoulder peak at 285 nm was observed in the UV-vis spectrum of Re-Ti-MWW because of the presence of hexa-coordinated Ti species [Figure 1C (b)]. The four titanosilicates all exhibited typical N_2 adsorption-desorption isotherms of microporous structures [Figure 1D]. The specific surface area and micropore pore volume of Ti-MWW were 555 $m^2 \cdot g^{-1}$ and 0.17 $cm^3 \cdot g^{-1}$, respectively. The specific surface area and micropore pore volume of Re-Ti-MWW significantly reduced to 64 $m^2 \cdot g^{-1}$ and 0.01 $cm^3 \cdot g^{-1}$, respectively [Supplementary Table 1], owing to the partial pore-blocking by the occluded PI molecules. TS-1 and Ti-MOR exhibited similar specific surface areas (440-450 $m^2 \cdot g^{-1}$) and micropore pore volumes (0.15-0.16 $cm^3 \cdot g^{-1}$).

Catalytic performance of different titanosilicates in AAL epoxidation

The epoxidation activity of four different zeolites was evaluated in the AAL epoxidation using MeCN as the solvent [Table 1]. Re-Ti-MWW displayed higher AAL conversion of 56.9% and H_2O_2 utilization efficiency

Table 1. Catalytic results of four titanosilicates in AAL epoxidation[a]

Catalyst	Si/Ti[b]	AAL conv. (%)	GLY sel. (%)	H$_2$O$_2$(%)		TOF[c]	D/r^2 (10^{-7} s^{-1})[d]
				conv.	eff.		
Ti-MWW	39	34.7	99.2	39.3	88.2	1,680	20.1
Re-Ti-MWW	39	56.9	99.4	58.6	97.1	2,754	466.0
TS-1	35	8.7	97.9	10.5	82.9	380	3.2
Ti-MOR	38	2.0	99.3	4.1	48.8	94	6.8

[a]Reaction conditions: catalyst, 0.03 g; allyl alcohol, 30 mmol; H$_2$O$_2$ (30 wt%), 30 mmol; MeCN, 5 mL; temperature, 313 K; time, 0.5 h; [b]Determined by ICP analysis; [c]TOF represented the accumulated number of allyl alcohol molecules converted per Ti site per hour; [d]Calculated from the data shown in Figure 3B. AAL: Allyl alcohol; GLY: glycidol; TOF: turnover frequency.
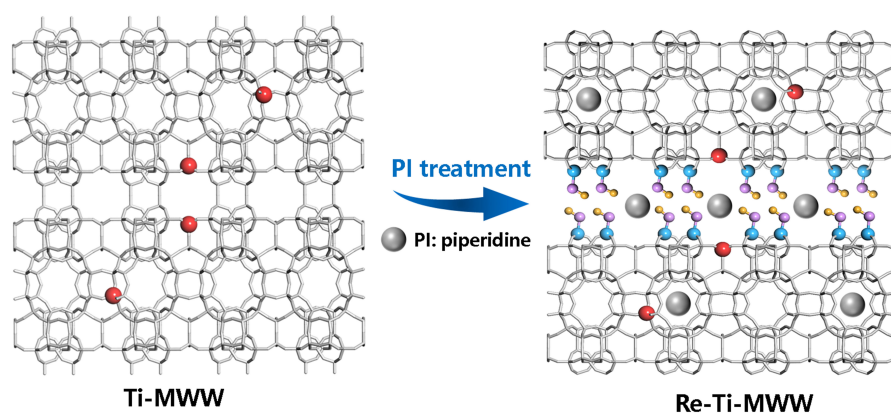
Scheme 1. PI-assisted structural rearrangement of Ti-MWW to Re-Ti-MWW. PI: Piperidine.

of 97.1% compared to Ti-MWW (34.7% and 88.2%, respectively). TS-1 and Ti-MOR showed significantly lower catalytic activity, with AAL conversion of 8.7% and 2.0%, respectively. All catalysts showed high GLY selectivity of > 97%. Considering that these titanosilicates contain different Ti contents, their catalytic activities were further compared by turnover frequency (TOF). The TOF value of Ti-MWW (1,680) was much higher than those of TS-1 (380) and Ti-MOR (94). The TOF value of Re-Ti-MWW was elevated to 2,754 after the PI-assisted 3D-2D structural transformation of Ti-MWW. Ti-MOR exhibited the lowest catalytic activity for the AAL epoxidation. The poor activity of Ti-MOR has also been reported in the epoxidation of other olefins[16], suggesting that Ti-MOR is not suitable for olefin epoxidation, although it exhibits excellent catalytic activity in aldehydes and ketones ammonia oxidation reactions[18]. The lower activity of medium-pore TS-1 compared to Ti-MWW was probably ascribed to the poor diffusion. Methanol was reported to be the preferred solvent for TS-1 in alkene epoxidation reactions, so the usage of MeCN solvent may also induce the lower activity of TS-1[17].

Effects of solvent on AAL epoxidation

As described above, the catalytic performance was first compared in MeCN solvent, but different titanosilicate catalysts may have distinct solvent effects[15]. Thus, the epoxidation activity of four zeolites was further evaluated in various solvents [Table 2]. For Ti-MWW zeolite, the AAL conversion of 34.7% in MeCN was higher than that in other protic solvents, suggesting that the most suitable solvent was MeCN, consistent with the previous report[13]. Meanwhile, the GLY selectivity of 99.2% in MeCN was also higher than those in protic solvents, because hydrolysis and alcoholysis easily occur in water and methanol solvents, respectively. For hydrophobic TS-1, the preferred solvent effect was methanol, although the activity of the TS-1 catalyst remained poor in methanol compared to Ti-MWW. The catalytic activity of

Table 2. Catalytic results of AAL epoxidation over titanosilicates in various solvents[a]

Catalyst	Solvent	AAL conv. (%)	GLY sel. (%)	H_2O_2 (%)	
				conv.	eff.
Ti-MWW	H_2O	30.5	96.8	32.8	92.9
	MeCN	34.7	99.2	39.3	88.2
	MeOH	13.7	90.4	22.8	60.1
	t-BuOH	19.6	98.5	22.7	86.3
Re-Ti-MWW	H_2O	98.1	99.1	98.5	99.5
	MeCN	56.9	99.4	58.6	97.1
	MeOH	67.4	95.1	72.1	93.5
	t-BuOH	42.5	99.2	48.3	87.9
TS-1	H_2O	10.3	95.4	13.4	76.9
	MeCN	8.7	97.9	10.5	82.9
	MeOH	14.5	88.4	19.4	74.7
	t-BuOH	6.3	97.1	8.7	72.4
Ti-MOR	H_2O	2.3	99.5	4.7	48.9
	MeCN	2.0	99.3	4.1	48.8
	MeOH	1.7	99.1	3.4	50.0
	t-BuOH	1.9	99.4	4.3	44.2

[a]Reaction conditions: catalyst, 0.03 g; allyl alcohol, 30 mmol; H_2O_2 (30 wt%), 30 mmol; solvent, 5 mL; temperature, 313 K; time, 0.5 h. AAL: Allyl alcohol; GLY: glycidol.

Ti-MOR was found to be low in all the solvents. The AAL conversion and GLY selectivity both increased for the Re-Ti-MWW catalyst compared to Ti-MWW in all the investigated solvents. In contrast to Ti-MWW, the epoxidation activity of Re-Ti-MWW was higher in protic solvent than that in aprotic MeCN. The AAL conversion and GLY selectivity in H_2O solvent increased from 30.5% to 98.1% and 96.8% to 99.1%, respectively, when the catalyst was changed from Ti-MWW to Re-Ti-MWW. Thus, the preferred solvent was H_2O for Re-Ti-MWW. Meanwhile, the enhancement of epoxidation performance was more significant in H_2O than that in MeCN when comparing the performance of Re-Ti-MWW to that of Ti-MWW.

The dependence of AAL conversion and GLY selectivity on reaction time between Ti-MWW and Re-Ti-MWW in the two solvents of H_2O and MeCN were also compared. With the reaction time proceeding, Re-Ti-MWW always showed higher AAL conversion in H_2O solution [Figure 2A], further indicating that the most suitable solvent was H_2O for Re-Ti-MWW. In terms of GLY selectivity, Re-Ti-MWW in both H_2O and MeCN and Ti-MWW in MeCN could kept almost intact within 120 min. However, the GLY selectivity of Ti-MWW in H_2O decreased from 98.4% to 94.1% after 120 min. In the AAL epoxidation reaction system, the main product is GLY, but the presence of weak acidic sites originating from Ti-OH, Si-OH, and Ti-OOH groups in titanosilicates may catalyze the hydrolysis of GLY to produce glycerol [Supplementary Scheme 2]. If MeOH or *t*-BuOH is used, GLY may also undergo alcoholysis to produce alcohol ethers. The ring-opening of GLY due to hydrolysis in H_2O and MeCN solvent was investigated over Ti-MWW and Re-Ti-MWW [Supplementary Figure 2]. The conversion of GLY was 19% and 3% after 5 h for Ti-MWW and Re-Ti-MWW in H_2O solvent, respectively, indicating that the hydrolysis was significantly prohibited over Re-Ti-MWW. The hydrolysis of GLY was also suppressed over Re-Ti-MWW in MeCN solvent. The neutralization of the weak acidity by the alkaline PI molecules was supposed to be the main reason for preventing the ring-opening side reactions[15]. It was also the reason for the decrease of GLY selectivity over Ti-MWW in H_2O solvent shown in Figure 2B.
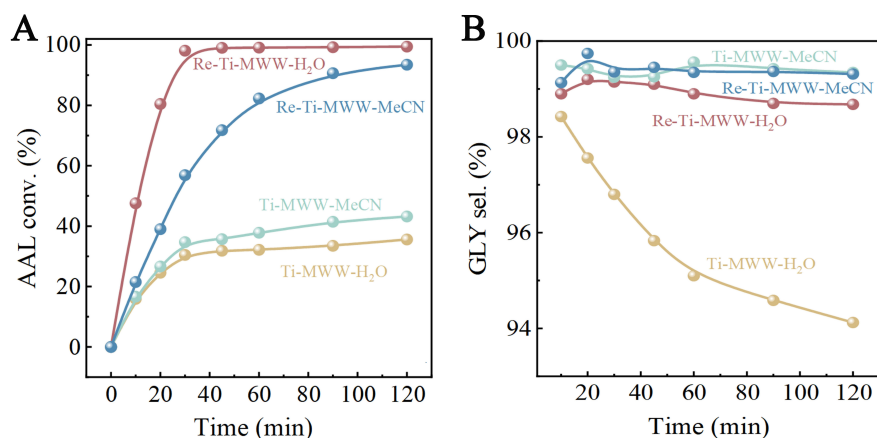
Figure 2. (A) AAL conversion and (B) GLY selectivity of AAL epoxidation with different reaction times over Ti-MWW and Re-Ti-MWW in solvent H_2O and MeCN. Reaction conditions: catalyst, 0.03 g; allyl alcohol, 30 mmol; H_2O_2 (30 wt%), 30 mmol; solvent, 5 mL; temperature, 313 K; time, 5-120 min. The labels in this figure represent "sample name-solvent". AAL: Allyl alcohol; GLY: glycidol.

The transformation of some tetrahedrally coordinated Ti species into open-site hexa-coordinated Ti species during PI rearrangement treatment was considered as the main reason for the enhanced activity of Re-Ti-MWW compared to Ti-MWW in our previous studies[15-17]. In fact, the transformation from 3D Ti-MWW zeolite to the corresponding 2D layered Re-Ti-MWW zeolite induced the formation of numerous surface Si-OH groups, which may change the framework hydrophilicity/hydrophobicity and then the adsorption behavior of AAL substrate. The adsorption ability of AAL over four different titanosilicates was first compared [Figure 3A]. The higher adsorption amount of AAL was observed over Ti-MWW (0.197 mmol·g^{-1}) in comparison to TS-1 (0.195 mmol·g^{-1}) and Ti-MOR (0.074 mmol·g^{-1}). However, the adsorption amount of AAL over Re-Ti-MWW was the lowest (0.061 mmol·g^{-1}) because the pores were blocked by PI molecules, consistent with decreased surface area and pore volume in Supplementary Table 1. The total adsorbed amount does not reflect the relative diffusion rate of the substrate[36]. Hence, the relative diffusion rate (D/r^2) was further calculated according to Fick's second law to precisely compare the adsorption behavior. The initial adsorption data in the first 10 s was used in the calculation [Supplementary Figure 3], because it was insensitive to the heat of adsorption[36]. The relative diffusion rate of AAL over Re-Ti-MWW was up to 466 × 10^{-7} s^{-1}, which was much larger than those of other zeolites [Figure 3B], although the pore volume was the smallest and the adsorption amount of AAL was the lowest. Thus, the pore opening was not the major factor that affected the relative diffusion rate of AAL. Given that AAL was quite hydrophilic, we considered the hydrophilicity/hydrophobicity of the zeolite affects the relative diffusion rate. The H_2O adsorption isothermal curve at 298 K and contact angle technique were used to characterize the hydrophobicity of the four titanosilicates [Figure 3C and D]. The relative H_2O-adsorption amount in Figure 3C was defined as the ratio of H_2O-adsorption volume to total pore volume. Re-Ti-MWW showed the largest relative H_2O-adsorption amount and the smallest contact angle, indicating that its hydrophilicity was the highest. We speculated that the formation of numerous Si-OH groups on MWW layer surface upon 3D to 2D structural transformation was the main reason for the hydrophilicity enhancement of Re-Ti-MWW compared to Ti-MWW. Therefore, the more hydrophilic Re-Ti-MWW zeolite with abundant Si-OH groups favors the rapid adsorption of hydrophilic AAL molecules. According to previous reports in the literature, the faster relative diffusion rate was favorable for higher activity in the initial reaction stage[36]. Thus, in addition to the formation of higher active Ti sites in Re-Ti-MWW, the increase of hydrophilicity was also a main reason for the enhancement of catalytic performance in AAL epoxidation using H_2O as the solvent. Moreover, the enhancement of hydrophilicity may also induce the change of solvent effect, resulting in H_2O as the preferred solvent for Re-Ti-MWW.
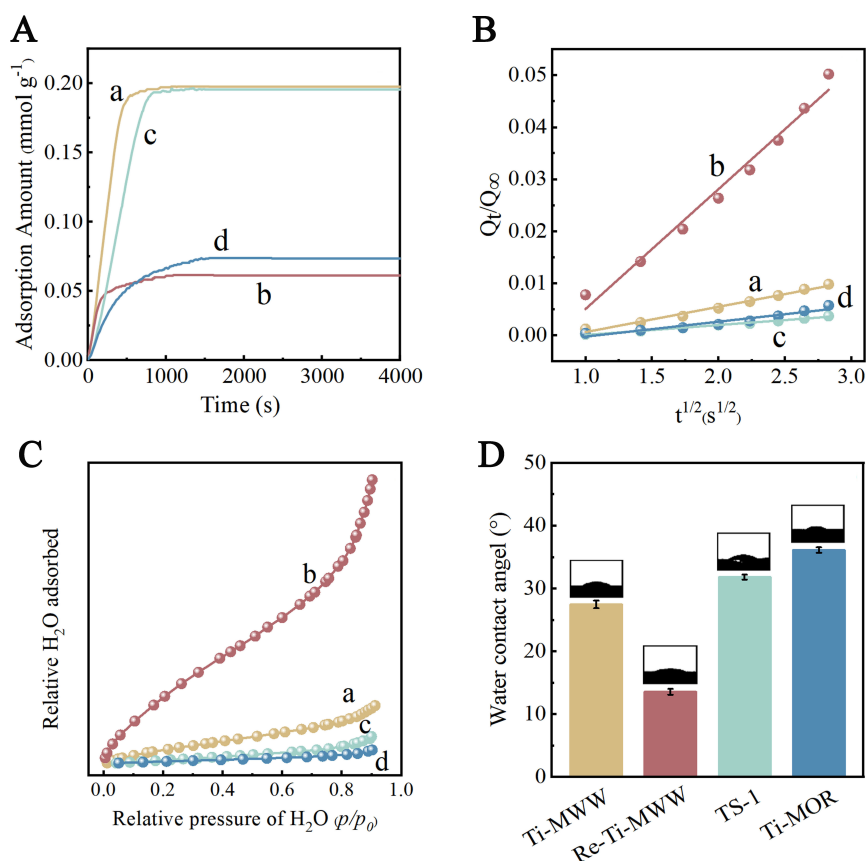
Figure 3. (A) Adsorption isotherms and (B) relative adsorption uptake of AAL over four titanosilicates at 313 K; (C) H_2O adsorption isotherms and (D) contact angle test of (a) Ti-MWW, (b) Re-Ti-MWW, (c) TS-1, and (d) Ti-MOR. AAL: Allyl alcohol.

Reaction kinetics of AAL epoxidation over Ti-MWW and Re-Ti-MWW

The epoxidation process catalyzed by the titanosilicates/H_2O_2 system proceeds in two steps. The first step is the activation of H_2O_2 on the Ti activity centers to generate Ti-O_α-O_β-H intermediates [Scheme 2][37], which is the rate-determining step of the entire epoxidation process. In the second step, the more electrophilic O_α in the intermediate interacts with the C=C in the olefins to realize the transfer of O_α, producing the epoxides. Therefore, the efficient generation of intermediate Ti-OOH is the key to the improvement of catalytic activity. The ability of Ti-OOH formation was compared between Ti-MWW and Re-Ti-MWW in different solvents. Figure 4A and B showed the relationship between the initial epoxidation rate and H_2O_2 concentration. A similar variation trend was observed for Ti-MWW and Re-Ti-MWW in both H_2O and MeCN solvents. The epoxidation rate increased with increasing H_2O_2 concentration at lower H_2O_2 concentration, indicating that Ti-OOH species were unsaturated. Therefore, at lower H_2O_2 concentration, the epoxidation rate depended on the rate of Ti-OOH formation, and the effect of solvent on H_2O_2 activation would affect the Ti-OOH formation and epoxidation rate. Re-Ti-MWW zeolite showed a higher epoxidation rate in H_2O compared to MeCN at lower H_2O_2 concentration, indicating H_2O favored the Ti-OOH formation. For the Ti-MWW catalyst, the epoxidation rate in MeCN was higher than that in H_2O, revealing that MeCN favored the formation of Ti-OOH. At higher H_2O_2 concentration, H_2O_2 concentration did not affect the epoxidation rate; thus, the reaction can be considered as pseudo zero-order reaction. The reaction order of was calculated at lower H_2O_2 concentration region [Figure 4C and D]. The reaction orders were 0.913 and 0.201 for Ti-MWW and Re-Ti-MWW in H_2O solvent, and they were 0.633 and 0.288 for the MeCN solvent, respectively. The smaller reaction order of H_2O_2 indicates better catalytic performance in the
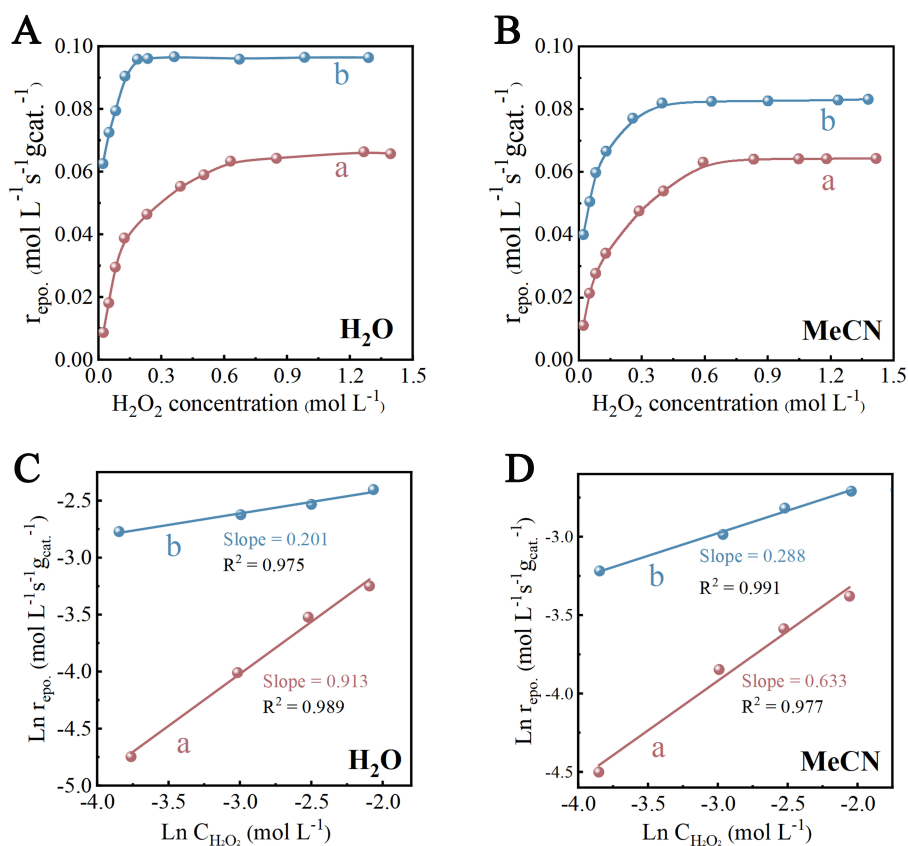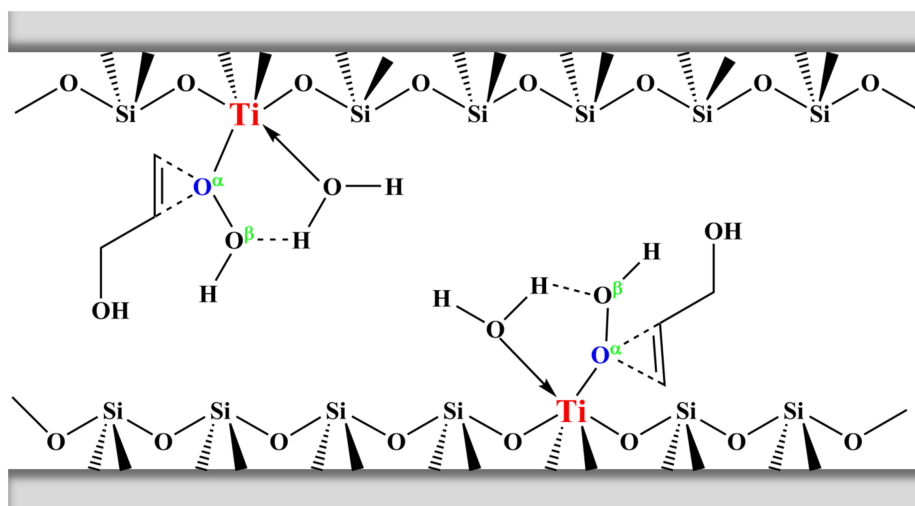
Figure 4. Dependence of AAL epoxidation rate on (A) H_2O_2 concentration and (B) over (a) Ti-MWW and (b) Re-Ti-MWW; H_2O_2 concentration and initial reaction rate (C) and (D) in H_2O and MeCN. Reaction conditions: catalyst, 0.03 g; allyl alcohol, 30 mmol; H_2O or MeCN, 5 mL; temperature, 313 K. AAL: Allyl alcohol.

Scheme 2. Ti-O_α-O_β-H intermediates generated by the activation of H_2O_2.

epoxidation reaction[38]. Re-Ti-MWW showed the lowest reaction order of H_2O_2 in H_2O solvent, consistent with the highest catalytic activity of Re-Ti-MWW in catalyzing AAL epoxidation reaction using H_2O solvent [Figure 2A].

Continuous epoxidation reaction of AAL over Re-Ti-MWW in H$_2$O solvent

Effects of reaction conditions

The continuous liquid-phase AAL epoxidation catalyzed by Re-Ti-MWW in H$_2$O solvent was carried out in a slurry bed reactor. The effects of reaction temperature, weight hourly space velocity (WHSV) of H$_2$O$_2$, AAL/H$_2$O$_2$ molar ratio, catalyst amount, and stirring speed on the performance of AAL epoxidation were investigated in detail. The effect of reaction temperature on the catalytic performance of Re-Ti-MWW in continuous AAL epoxidation reaction was shown in Figure 5A. The H$_2$O$_2$ conversion improved from 96.5% to almost 100% when the reaction temperature increased from 303 to 313 K, although H$_2$O$_2$ effective utilization and GLY selectivity were kept stable at 92.5% and 96.8%, respectively. The effective utilization of H$_2$O$_2$ and GLY selectivity dropped as the reaction temperature was further increased to 323 K. However, the H$_2$O$_2$ conversion remained constant. Although increasing the reaction temperature favored the epoxidation reaction, the ineffective decomposition of H$_2$O$_2$ and the pore-opening reaction of GLY were also enhanced. Thus, the optimum initial operating temperature for the continuous liquid-phase AAL epoxidation was set at 313 K.

The higher WHSV of H$_2$O$_2$ could increase the GLY concentration in the reaction mixture under the condition that H$_2$O$_2$ is completely consumed. With the WHSV of H$_2$O$_2$ setting at 0.3 h^{-1}, the H$_2$O$_2$ conversion, H$_2$O$_2$ effective utilization, and GLY selectivity were 99.4%, 93.6%, and 97.2%, respectively [Figure 5B]. Increasing the WHSV of H$_2$O$_2$ to 0.4 h^{-1}, the H$_2$O$_2$ conversion was not changed while the H$_2$O$_2$ effective utilization and GLY selectivity slightly decreased. When the WHSV of H$_2$O$_2$ was further increased to 0.5 h^{-1}, the H$_2$O$_2$ effective utilization and GLY selectivity declined to 85.2% and 92.5%, respectively. Higher WHSV of H$_2$O$_2$ induced higher H$_2$O$_2$ concentration in the reaction solution, which increased the acidity and then aroused inefficient decomposition of H$_2$O$_2$ and ring-opening of GLY. Hence, the preferred WHSV of H$_2$O$_2$ was determined to be 0.4 h^{-1}.

Although the theoretical AAL/H$_2$O$_2$ ratio is 1 in the epoxidation of AAL with H$_2$O$_2$ as the oxidant, the AAL/H$_2$O$_2$ molar ratio should be greater than 1 in the actual production process to consume all the H$_2$O$_2$ in the system for safety. With the AAL/H$_2$O$_2$ molar ratio of 1, the H$_2$O$_2$ conversion was only 97.1% [Figure 5C]. The H$_2$O$_2$ conversion reached 99.3% when the molar ratio of AAL/H$_2$O$_2$ was raised to 1.5. Further increasing the AAL/H$_2$O$_2$ ratio hardly changed the H$_2$O$_2$ conversion. Thus, the AAL/H$_2$O$_2$ ratio of 1.5 was enough for the complete consumption of H$_2$O$_2$.

The effect of catalyst amount was also investigated [Figure 6A]. Increasing the catalyst amount favored the conversion of H$_2$O$_2$, while the effective utilization of H$_2$O$_2$ and GLY selectivity were decreased. It is conceivable that increasing the catalyst amount raised the content of acid centers, which intensified the ineffective decomposition of H$_2$O$_2$ and ring-opening of GLY. The catalyst amount of 1 g was enough because the complete conversion of H$_2$O$_2$ can be realized. By changing the stirring speed, the influence of external diffusion can be eliminated. In Figure 6B, although the increase of stirring speed increased the H$_2$O$_2$ conversion, the ineffective decomposition of H$_2$O$_2$ was also enhanced. Therefore, 500 rpm was chosen as the optimal stirring speed.

Evaluation of catalyst lifetime

The catalytic performance of Re-Ti-MWW in continuous AAL epoxidation using water and acetonitrile solvent was compared [Figure 7]. The lifetime of Re-Ti-MWW in water solvent reached 121 h, with the average H$_2$O$_2$ conversion, H$_2$O$_2$ effective utilization, GLY selectivity, and GLY yield of 98.1%, 91.1%, 96.3%,
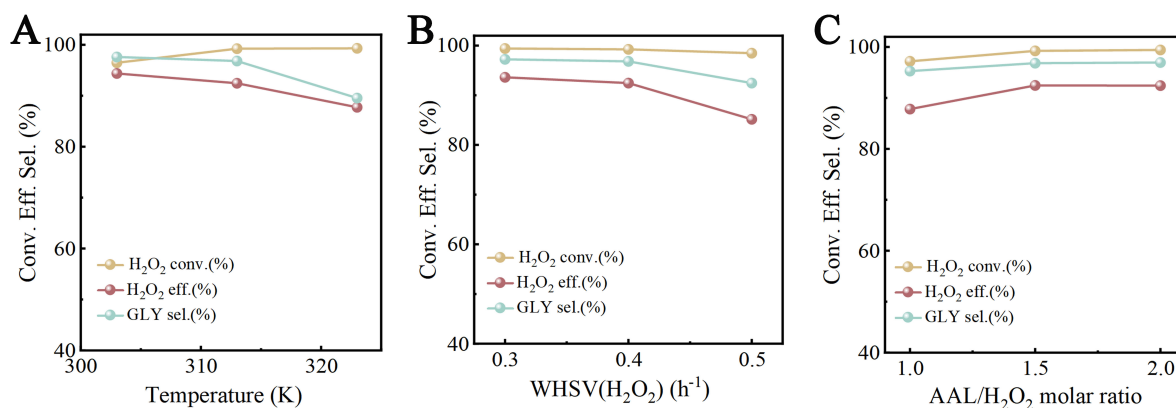
Figure 5. (A) Effects of temperature, (B) WHSV of H_2O_2, and (C) AAL/H_2O_2 molar ratio on the epoxidation of AAL over Re-Ti-MWW. Reaction conditions: catalyst, 1 g; temperature 313 K; AAL/H_2O_2 molar ratio, 1.5 (A and B); H_2O/AAL mass ratio, 4; WHSV(H_2O_2) = 0.4 h^{-1} (A and C); 500 rpm. The data were the average values at 45 h after the reaction reached a steady state. WHSV: Weight hourly space velocity; AAL: allyl alcohol.
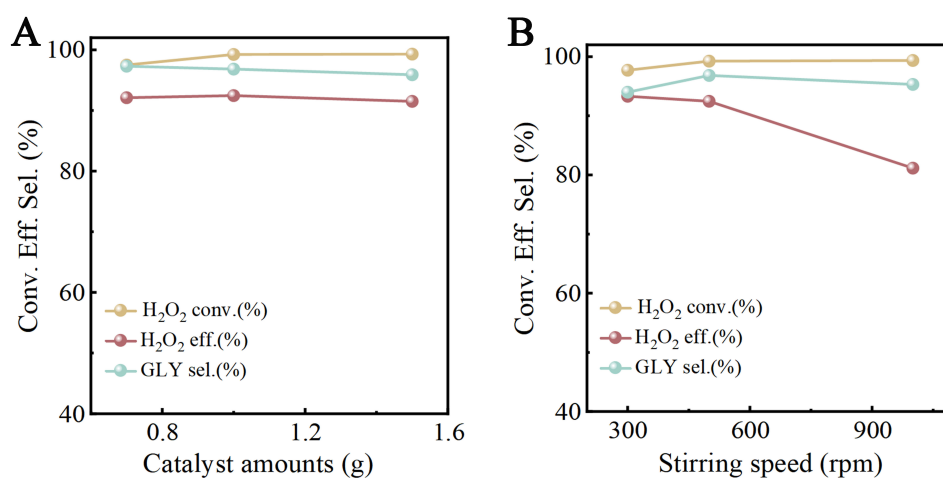

Figure 6. Effects of (A) catalyst amounts and (B) stirring speed on the epoxidation of AAL over Re-Ti-MWW. Reaction conditions: catalyst, 1 g (for Figure 6B); temperature, 313 K; AAL/H_2O_2 molar ratio, 1.5; H_2O/AAL mass ratio, 4; WHSV(H_2O_2) = 0.4 h^{-1}; 500 rpm (for Figure 6A). The data were the average values at 45 h after the reaction reached a steady state. AAL: Allyl alcohol; WHSV: weight hourly space velocity.

and 86.0%, respectively. The H_2O_2 conversion was maintained at 99% at 313 K for 30 h. After that, the H_2O_2 conversion started to decrease and the temperature was increased to maintain a high H_2O_2 conversion (> 99%) until the temperature was increased to 323 K. The catalytic lifetime of Re-Ti-MWW was much higher than that of Ti-MWW (13 h) in water [Supplementary Figure 4]. The average H_2O_2 conversion was only 96% for Re-Ti-MWW when MeCN was used as the solvent, and the reaction duration was shortened to 110 h, while the selectivity of GLY was raised to 99.1% compared to the H_2O system. Acetonitrile, as a weak basic solvent, reduced the acidity of the reaction system, thus inhibiting the side reactions. Therefore, adding some alkaline additive may help to increase the GLY selectivity for AAL epoxidation in H_2O solvent and further increase the lifetime.

As shown in Figure 8A, the lifetime increased to 163 h when 5 ppm of $(NH_4)_2CO_3$ was added to the reaction feedstock. The GLY selectivity increased from 96.3% to 97.3%. However, introducing the alkaline species in
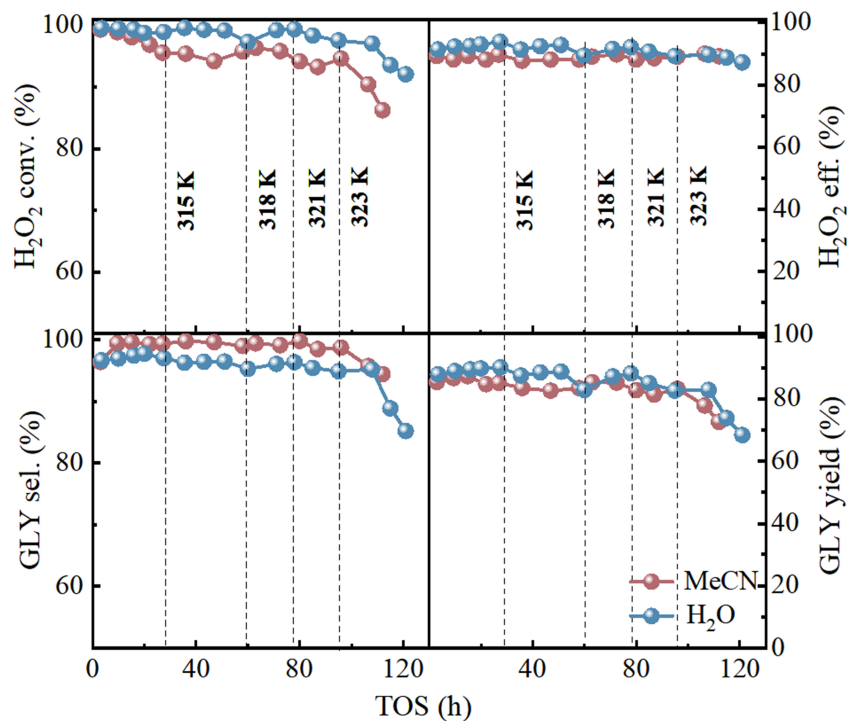
Figure 7. The lifetime of Re-Ti-MWW in the epoxidation of AAL. Reaction conditions: catalyst, 1 g; temperature, 313-323 K; AAL/H_2O_2 molar ratio, 1.5; solvent/AAL mass ratio, 4; WHSV(H_2O_2) = 0.4 h^{-1}; 500 rpm. AAL: Allyl alcohol; WHSV: weight hourly space velocity.
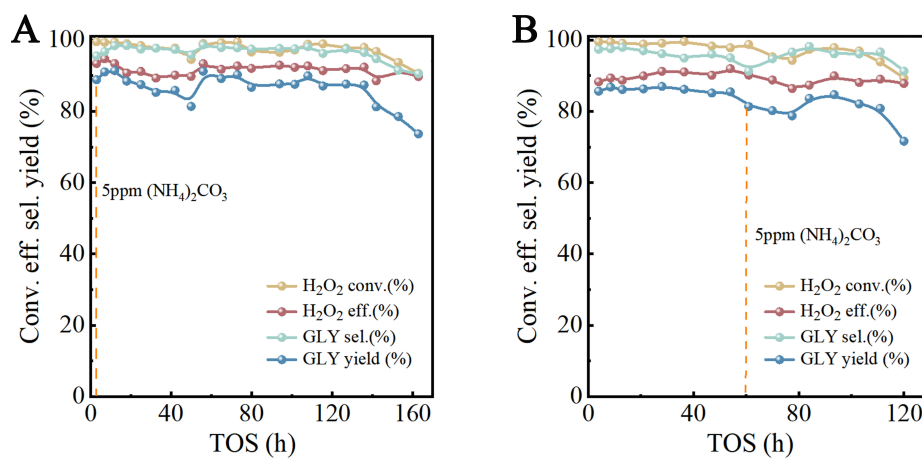

Figure 8. Effect of ammonia (A) before and (B) after addition on epoxidation of AAL. Reaction conditions: catalyst, 1 g; $(NH_4)_2CO_3$ amounts, 5 ppm; temperature, 313-323 K; AAL/H_2O_2 molar ratio, 1.5; H_2O/AAL mass ratio, 4; WHSV(H_2O_2) = 0.4 h^{-1}; 500 rpm. AAL: Allyl alcohol; WHSV: weight hourly space velocity.

the middle stage of the reaction was less effective [Figure 8B], indicating that the ring-opening of GLY reaction should be prohibited in the early stage, because the by-product glycerol was hardly removed once they are formed.

CONCLUSIONS

Re-Ti-MWW catalyst with higher hydrophilicity was obtained by PI rearrangement treatment and showed higher catalytic activity in AAL epoxidation reaction than Ti-MWW. High relative diffusion rates of AAL and the formation of more active open-site hexa-coordinated Ti species resulted in increased catalytic activity in AAL epoxidation reaction. Meanwhile, the most suitable solvent was changed from MeCN for Ti-MWW to H_2O for Re-Ti-MWW. Re-Ti-MWW showed superior H_2O_2 activation ability in H_2O solvent than in MeCN solvent. Using the green solvent of H_2O, the lifetime of Re-Ti-MWW in continuous AAL epoxidation reaction was up to 163 h, and the selectivity of GLY was maintained at 97%.

DECLARATIONS

Authors' contributions
Conception and design of the study: Wu P, Xu H
Data collection and analysis: Gong X
Sample preparation: Tuo J, Wang J, Li X, Zhai C
Paper writing and reviewing: Gong X, Xu H, Wu P

Availability of data and materials
Not applicable.

Financial support and sponsorship

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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