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# Environmental-Friendly Catalytic Oxidation Processes Based on Hierarchical Titanium Silicate Zeolites at SINOPEC

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Additional information is available at the end of the chapter

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## Abstract

Since it was claimed by EniChem in 1983 for the first time, titanium silicate-1 (TS-1) zeolite presented the most delightful catalytic performance in the area of selective organic oxidation reactions. To enhance the mass diffusion property, hierarchical titanium silicate with hollow cavities within crystal was prepared by using a post-synthesis treatment in the presence of organic template, and then, it was commercially produced and employed in many industrial catalytic oxidation processes, such as propylene epoxidation, phenol hydroxylation, and cyclohexanone ammoximation. Moreover, we also developed several totally novel oxidation reactions on hollow titanium silicate (HTS) zeolite, i.e., Baeyer-Villiger oxidation of cyclohexanone and chlorohydration of allyl chloride with HCl and H<sub>2</sub>O<sub>2</sub>. In all cases, HTS shows much better catalytic performance than TS-1, attributing to the mass diffusion intensification by introducing hollow cavities. On the other hand, enormous works on synthesizing hierarchical TS-1 zeolites with open intracrystalline mesopores have been done via silanization treatment and recrystallization. Based on them, several bulk molecule oxidation processes with *tert*-butyl hydroperoxide, such as epoxidation of fatty acid methyl ester (FAME) and large olefins, have been carried out. As a consequence, hierarchical TS-1 zeolites supply a platform for developing environmental-friendly catalytic oxidation processes to remarkably overcome the drawbacks of traditional routes.

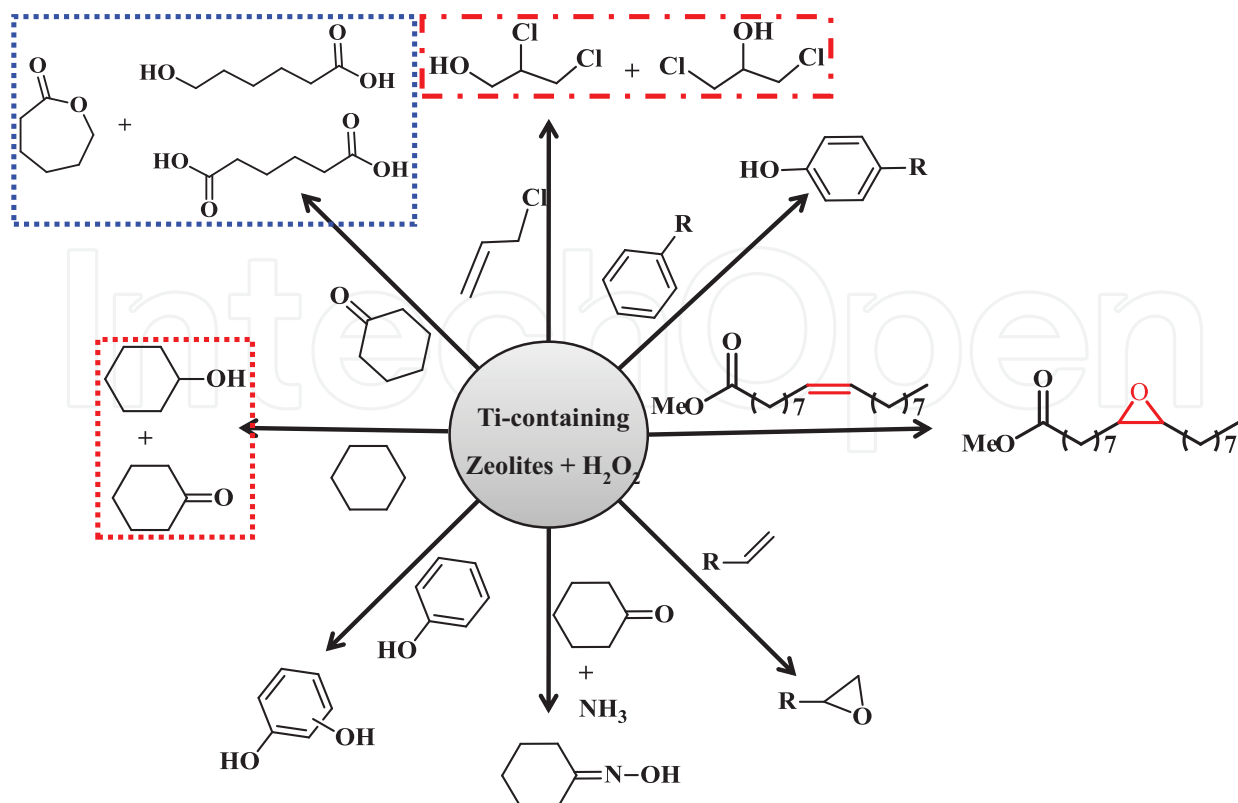
**Keywords:** titanium silicate zeolite, catalytic oxidation, novel chlorohydration process, HPPO, hierarchical structure, hydrogen peroxide

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## 1. Introduction

Framework-incorporated zeolite is an important kind of acid catalyst, which has already been successfully applied or shown great application potentials in many industrial processes in last 30 years [1–4]. Since the first claim of titanium silicate-1 (TS-1) zeolite by EniChem in 1983, serial of metal elements (such as Ti, Sn, Fe, V, Cr, Mn, Zr, Ga, and Ge) have been incorporated into the framework matrix of zeolite materials via the isomorphous substitution of Al atoms in crystalline aluminosilicates through different approaches [5–10]. When  $\text{Ti}^{4+}$ ,  $\text{Sn}^{4+}$ , and  $\text{Zr}^{4+}$  species incorporated into the framework of zeolites, basic subunits are neutral, without needing balancing by cation ions, thus no formation of Brønsted acid sites. However, these metal ions can accept shared electron pairs from electron-rich groups (i.e., peroxide, carbonyl, and C-C bonds) to make substrates much more reactive during catalytic reactions [11–13]. On the other hand, catalytic selective oxidation of hydrocarbons to produce oxygenated organic compounds is of great significance to give birth to chemical intermediates and fuels. Unfortunately, traditional oxidation approaches always suffer from using hazard reagents, complex operation, high energy and cost consumption, low product selectivity, and high pollution [14–16].

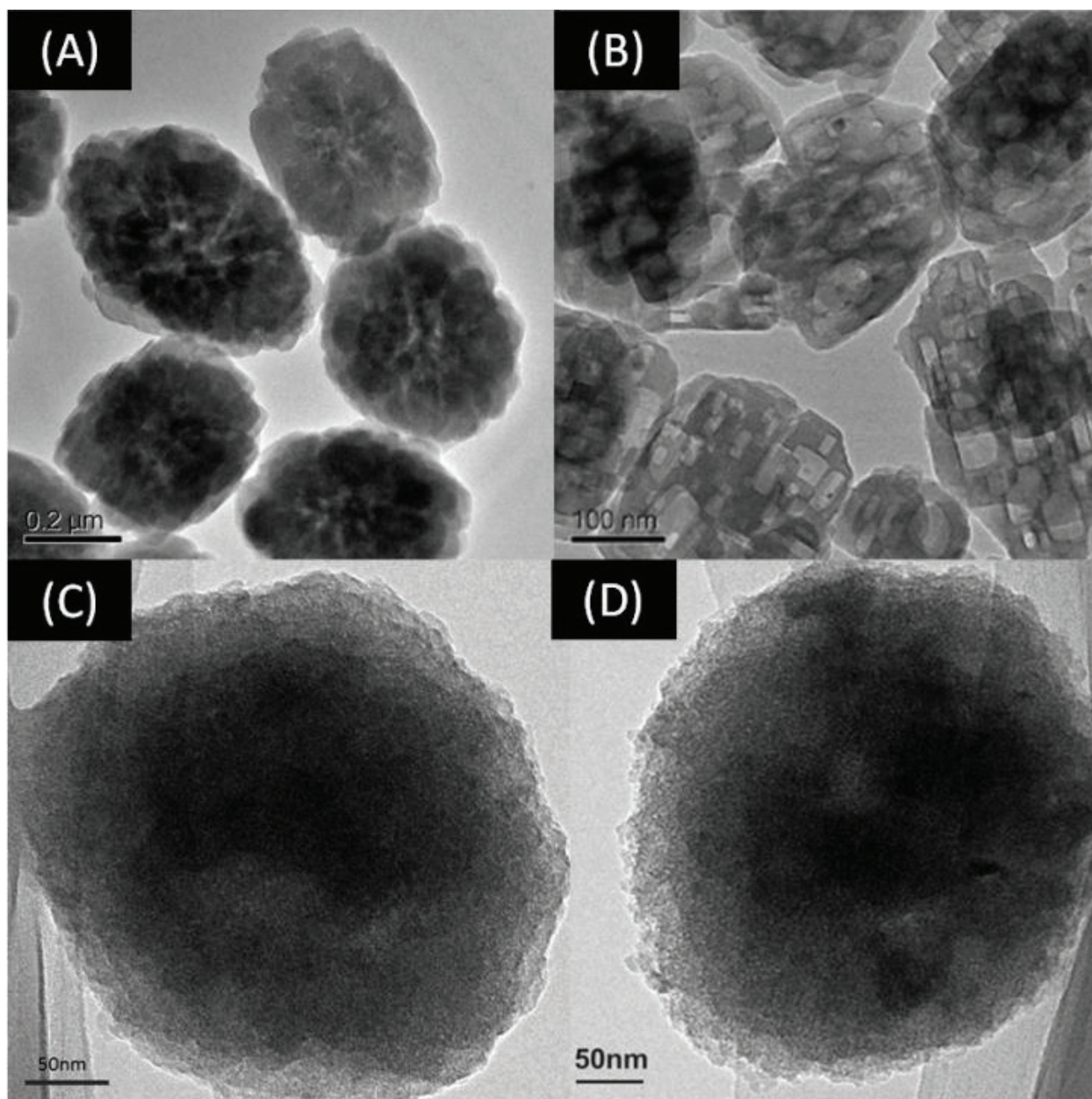
To avoid these drawbacks, heterogeneous catalysts (specially based on zeolites) have been introduced to develop highly efficient oxygenated hydrocarbons transformation due to their unique porosity and Lewis acidity for activating oxidants and/or substrates [17–19]. For example, in conventional route, cyclohexanone oxime is produced via a hydroxylamine method, which needs four steps, involving ammonia oxidation, production of hydroxylamine with liquid acids, cyclohexanone ammoximation, and decomposition of ammonium, generating a large amount of waste and side products [20–22]. In 1986, a totally novel “one-step” cyclohexanone ammoximation process with ammonia ( $\text{NH}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was developed by EniChem via using TS-1 zeolite as a catalyst under mild conditions, with water only as a by-product [23, 24]. Obviously, Ti-incorporated zeolites provide excellent opportunity to update the efficiency of oxidation processes. However, TS-1 zeolite suffered the limitations of mass diffusion, its narrow 10 member-ring channel [25–27]. Thus, a novel post-synthesis route to modify the traditional TS-1 was developed by the researchers at SINOPEC before 2000, obtaining the far more stable hollow titanium silicate (HTS) zeolite. It is worthy to note that HTS zeolite has been commercially manufactured by SINOPEC, and applied in several green catalytic oxidation processes, such as cyclohexanone ammoximation, phenol hydroxylation, and propylene epoxidation [28–30]. Moreover, several completely new reactions, such as chlorohydration of allyl chloride and Baeyer-Villiger oxidation of cyclohexanone, were initially developed on using HTS zeolite [31, 32]. In recent years, a spongy-like TS-1 zeolite with abundant of open mesopores was prepared via combining the silanization treatment and post-synthesis route under hydrothermal conditions. And it also found some bulk molecule oxidation reactions based on this hierarchical TS-1, such as epoxidation of methyl oleate and large olefins. Thus, this review will majorly summarize the application of hierarchical TS-1 we synthesized in the area of oxidation, as shown in **Figure 1**.



**Figure 1.** Catalytic oxidation reactions on hierarchical titanium silicate zeolite with  $\text{H}_2\text{O}_2$  as an oxidant under mild conditions.

## 2. Synthesis strategies of hierarchical titanium silicate zeolites

TS-1 zeolite was claimed by the researcher EniChem in 1983 for the first time, and then it attracted kind attentions from the world, owing to its pioneering role in exploiting metal-incorporated zeolites [4]. However, in the early years, the key factors for TS-1 zeolite synthesis were far beyond well understanding, thus it was hard to repeat the synthesis of TS-1 in parallel, even under the same conditions. That is ascribed to the different crystallization behaviors between Ti and Si precursors during hydrothermal synthesis processes. To overcome this major drawback, a post-synthesis method, involving the simultaneous dissolution of framework atoms and recrystallization of low aggregated species, was developed by M. Lin and coworkers at SINOPEC in the end of 1990s [33–35]. In a typical procedure, TS-1 was synthesized via the EniChem published method for the first time; and then it was calcined and treated by specific agents; in the end, TS-1 was recrystallized in the presence of SODs at high temperature with autogenous pressure. It has been confirmed that unique intracrystalline cavities (about several to several tens nm in size) are generated through post-treatment, and this material is referred to as hollow titanium silicate (HTS) zeolite, which is of much better diffusion property than TS-1, as shown in **Figure 2** [36]. On the other hand, recrystallization treatment promotes the increasing of framework Ti content, with the significant decreasing of framework defects (Si-OH and Ti-OH groups). Thus, HTS displays far higher stability than



**Figure 2.** Transmission electron microscopy images of TS-1 and hierarchical TS-1 zeolites : (A) TS-1, (B) HTS, (C) TS-OS, and (D) TS-SP.

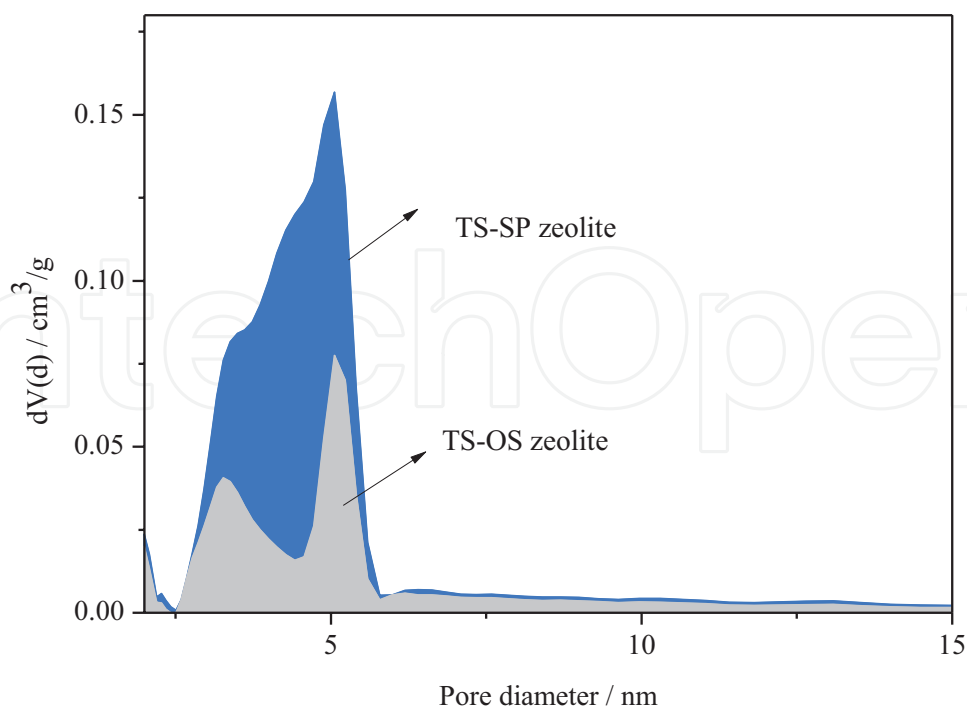
TS-1 during catalytic oxidation processes, especially in alkaline ammoximation reactions, due to high resistance to ammonia. Up to now, HTS zeolite had been already commercially manufactured at SINOPEC, and successfully applied in many selective catalytic oxidation processes, i.e., cyclohexanone ammoximation, propylene epoxidation, and phenol hydroxylation, presenting desirable economic and social benefits via reducing cost and waste production. To the best of our best knowledge, HTS is the first and only hierarchical titanium-based zeolite applied in industry, and the detailed synthesis, characterization, and application have been summarized in our previous chapter [37].

However, these cavities inside HTS zeolite cannot favor the accessibility of bulk organic molecules to inner tetrahedral framework Ti sites, owing to the 10-member ring pore mouth. To solve this problem, many attempts and efforts have been paid through introducing mesopores and/or macropores with zeolite particles, including selective removing framework-composite atoms, channel filling with soft or hard templates, reassembly of small crystals around mesopore templates, and adding amphiphilic organic surfactants and silicon sources. Among them, hierarchical TS-1 zeolite of rich open mesopores (remarked as TS-OS, as shown in **Figure 2C**) synthesized by introducing amphiphilic organic silane agents is considered as another potential industrial catalyst in the near future [38, 39]. It is very easy and available to synthesis TS-OS even in industry, just adding a few amount of organic silane agents, such as N-[3-(trimethoxysilyl) propyl]aniline and N,N-diethyl-3-(trimethoxysilyl) propan-1-amine, into conventional TS-1 synthesis mixture under hydrothermal conditions. That is attributed to the inhibition of crystal growth by organic silane groups inside particles, as Si-C bonds are ultrastable at high temperature. It is noted that silane groups are easily aggregated, thus mesopores are formed when the organic groups are removed by calcination in air at 550°C. Of course, compared with TS-1, TS-OS is of high mass transfer capability, allowing the entrance of bulk organic substrates and oxidants. Thus, TS-OS exhibits much better catalytic performance than TS-1 in some specific oxidations. It is worthy to mention that organic silane, usually serving as coupling agents for binder and coating, are very cheap and easily obtained in market, so it is available to synthesis of TS-OS at large scale.

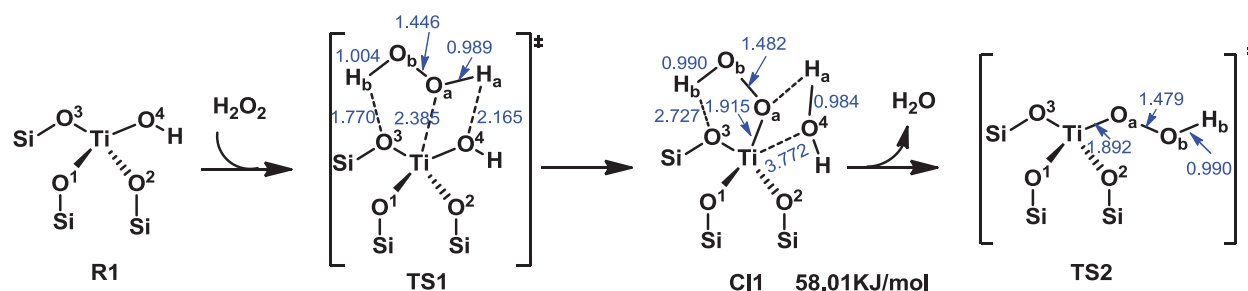
In addition, to make inner mesopores be more uniform, TS-OS zeolite was post-synthesized in the presence of long chain quaternary ammonium hydroxide (such as cetyltrimethylammonium hydroxide, CTAOH) under hydrothermal conditions, to give birth to spongy-like TS-1 zeolite (labeled as TS-SP), as shown in **Figure 2D**. As CTAOH can enter into the crystal of TS-OS along mesopores rather than micropores, the dissolution of framework atoms and reassembly of soluble Ti and Si species under the impact of CTAOH micelles with zeolite particles are simultaneously promoted during post-synthesis processing, thus forming the relatively uniform mesopores, as demonstrated in **Figure 3**. There are two peaks existed for TS-OS, the first one is ascribed to mesopores created by silane agents and the second one is related to intercrystalline mesopore among small crystal particles. The band for TS-SP is very narrow, suggesting the intracrystalline mesopores become much more uniform after reassembly.

### 3. Nature of the activating of H<sub>2</sub>O<sub>2</sub> molecules by TS-1 zeolite

As it is well known that TS-1 zeolite is an excellent catalyst via improving the nucleophilic attack capability of aqueous H<sub>2</sub>O<sub>2</sub> solution in catalytic oxidation reactions [40, 41]. When the H<sub>2</sub>O<sub>2</sub> molecules are adsorbed on the tetrahedral Ti active sites (**Figure 4**), the negative charges on both O<sub>a</sub> and O<sub>b</sub> atoms in TS2 are -0.460 and -0.476, respectively, which are of much stronger nucleophilic attack capability than that in H<sub>2</sub>O<sub>2</sub> molecules (about -0.426), as listed in **Table 1**. It indicates that the H<sub>2</sub>O<sub>2</sub> molecules are activated, with the formation of Ti-OOH species.



**Figure 3.** Pore-size distribution of TS-OS and TS-SP zeolites calculated by the nonlocal density function theory (NL-DFT) method.



**Figure 4.** Activation of  $\text{H}_2\text{O}_2$  molecules by tetrahedral framework Ti sites calculated by the density function theory (DFT) method.

#### 4. Chlorohydration of allyl chloride with HCl and $\text{H}_2\text{O}_2$ to produce dichloropropanol

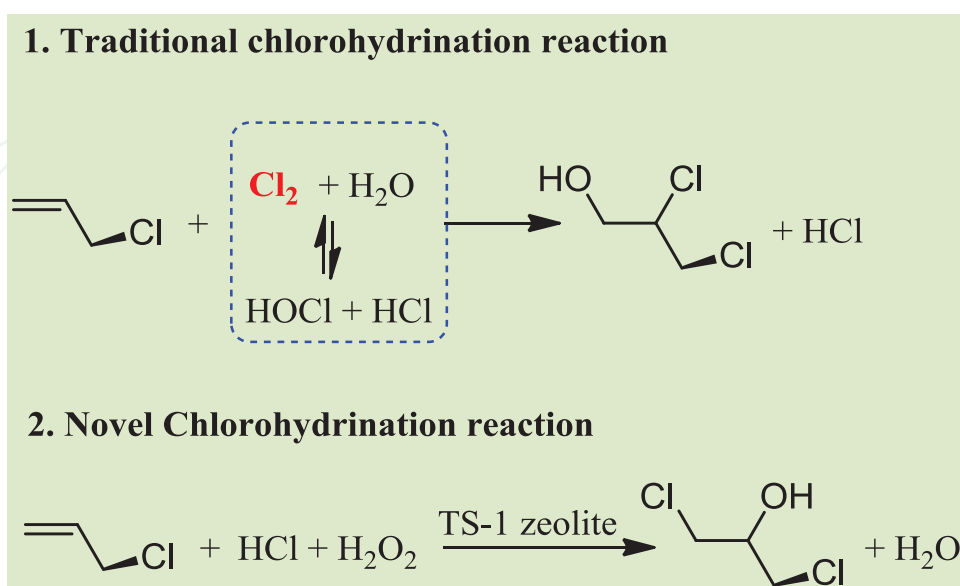
Recently, we have developed a totally novel route to prepare dichloropropanol (DCP) through the chlorohydration of allyl chloride (AC) with HCl and  $\text{H}_2\text{O}_2$  base on HTS as a catalyst, to replaced  $\text{Cl}_2$  and  $\text{H}_2\text{O}$  as raw materials in traditional route, as shown in **Scheme 1** [42]; that is, because  $\text{Cl}_2$  is highly hazard and harmful for environment and human health, and difficult to be stored and transfer, producing a large amount of waste. Most importantly, to avoid the production of trichloropropane (TCP), a great deal of water are added to reduce the concentration of  $\text{Cl}_2$  and its derivatives (HOCl and HCl), therefore causing the low content of DCP (<4 wt%) in final mixture [43, 44]. Obviously, the tradition  $\text{Cl}_2$  route goes against the principles

	Atoms	Before H <sub>2</sub> O <sub>2</sub> adsorption	After H <sub>2</sub> O <sub>2</sub> adsorption	Charge difference
H <sub>2</sub> O <sub>2</sub>	O <sub>a</sub>	-0.426	-0.460	-0.034
	O <sub>b</sub>	-0.426	-0.476	-0.050
	H <sub>a</sub>	0.426	0.410	-0.016
	H <sub>b</sub>	0.426	0.469	0.043

**Table 1.** Charge difference of TS-1 cluster and H<sub>2</sub>O<sub>2</sub> molecule before and after H<sub>2</sub>O<sub>2</sub> adsorption.

of green and sustainable chemistry, but HCl is very available and less harmful. It is surprisingly to observe that both AC conversion and DCP selectivity simultaneously over 95% under optimized reaction conditions, and DCP concentration is higher than 20 wt% in aqueous solution. Thus, this novel route demonstrates very excellent industrial potential, due to its high efficiency and low waste produced.

To study the mechanism of this route, different Ti-containing catalysts were evaluated by a novel chlorohydration reaction under almost the same condition, as shown in **Figure 5**. Among the catalysts we tested, HTS shows the highest AC conversion (over 85%), far higher than that of TS-1 (49%), owing to the improvement of mass diffusion through hierarchically closed mesopores within HTS zeolite particles. At the same time, HTS and TS-1 exhibit much higher selectivity (>88%) of DCP (including 1,3-DCP and 2,3-DCP) than other catalysts, suggesting tetrahedral framework Ti species help the formation of DCP. And the major product catalyzed by TS-1 and HTS is 1,3-DCP, while 2,3-DCP is mainly obtained via the traditional Cl<sub>2</sub> route. To explicate this phenomena, ring-opening reaction of epichlorohydrin (ECH) with HCl in aqueous solution had been carried out, with a 1,3-DCP selectivity higher than 98% and



**Scheme 1.** Comparison of traditional and novel chlorohydration reactions.



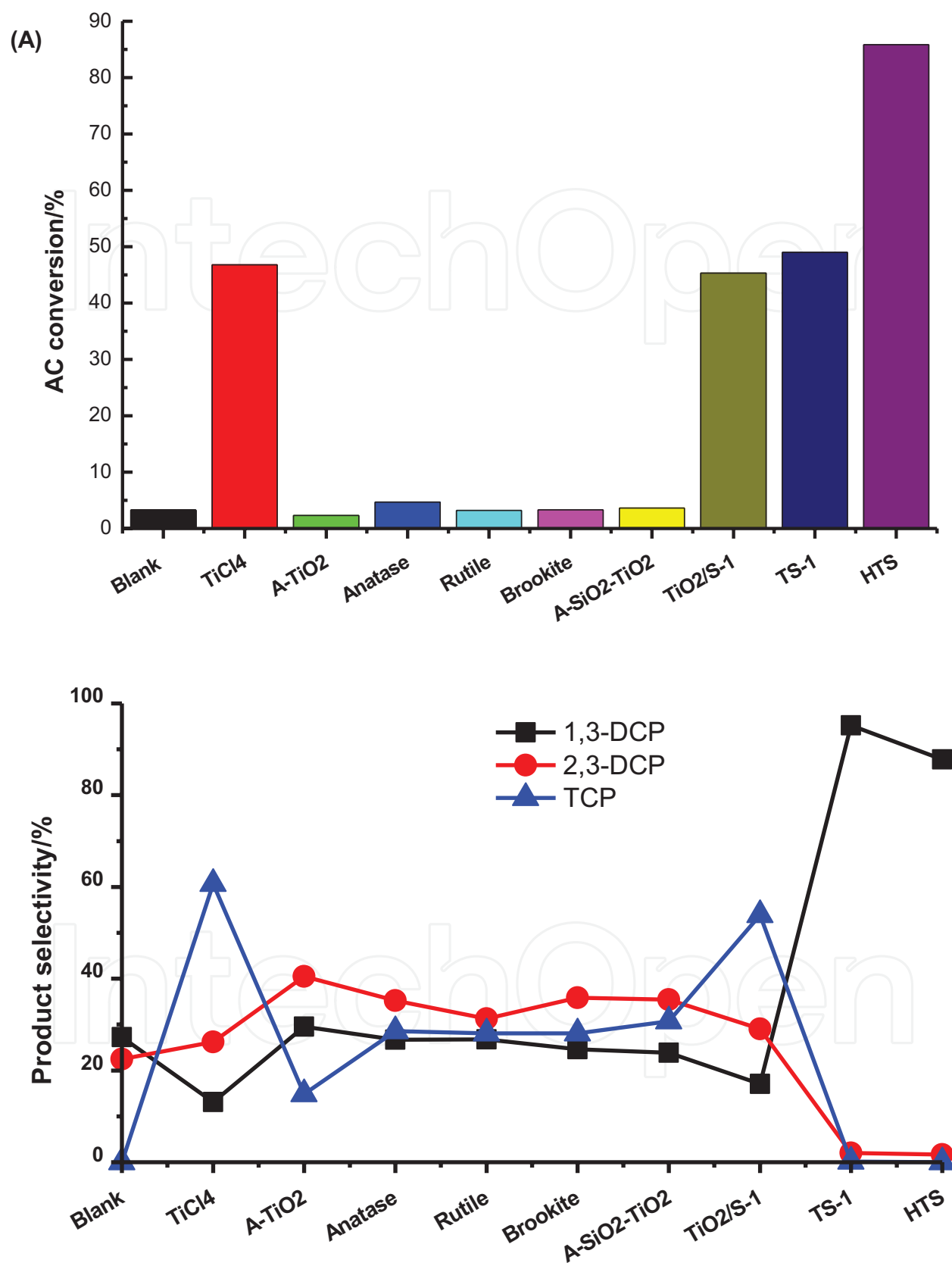


Figure 5. Catalytic performance of different Ti-based catalysts in novel chlorohydration of AC with HCl and H<sub>2</sub>O<sub>2</sub> under mild conditions: (A) AC conversion and (B) DCP selectivity.

complete AC conversion. In fact, TS-1 zeolite is of high catalytic activity in olefin epoxidation reaction, and many  $\text{H}_2\text{O}_2$  oxidized propylene epoxidation units (called HPPO process) have been established in global. However, TS-1 shows poor catalytic performance in the epoxidation of AC with  $\text{H}_2\text{O}_2$  due to the strong electron-withdrawing effect of Cl atoms on C=C bonds [45, 46]. However, in the presence of HCl, the epoxidation reaction can be accelerated, which is ascribed to the promotion of chemical balance to DCP via ring-opening reaction catalyzed by  $\text{H}^+$  species.

It is worthy to note that there are still many serious drawbacks related to the HPPO process, attributing to the side-products caused by  $\text{H}_2\text{O}$  [47, 48]. As a result, this route provides a novel method to prepare DCP, with high AC conversion and target product selectivity. Above all, it is indicated that the mechanism of this route lines in the first epoxidation of AC catalyzed by framework Ti species, and then ECH becomes ring opening with HCl. On the other hand,  $\text{Cl}_2$  and its derivatives (such as  $\text{Cl}_3^-$ , but no HOCl) are detected by UV-Raman spectroscopy (with an irradiation wavelength of 325 nm). It means that the  $\text{Cl}_2$ -based chlorohydration process can also be occurred in this route, similar as the traditional route, inferring that epoxidation of AC competes with the route of  $\text{Cl}_2$  [49–52]. What is more, there is only TCP generated catalyzed by HTS and TS-1 zeolites, which is relevant with the  $\text{Cl}_2$  formed via oxidation of HCl with  $\text{H}_2\text{O}_2$ , significantly increasing the utilization efficiency of AC to prepare DCP. Except for the desired catalytic activity and selectivity, HTS also gives much higher stability than TS-1 when they are treated by 37 wt% HCl solution at room temperature. It is found that, after 3 months treatment, HTS zeolite still remains as high AC conversion as fresh one, while the catalytic performance of TS-1 becomes fast decreasing when it was acidic treated for 5 days. As shown in **Figure 6**, HTS can be used six times in a novel chlorohydration route, without any decreasing of AC conversion and DCP selectivity, which is attributed to the reincorporation of Ti species into framework through post-synthesis treatment.

## 5. Ammoximation of ketones with $\text{H}_2\text{O}_2$ and $\text{NH}_3$

Ammoximation reaction is very important to produce oximes from ketones and aldehydes in industry [53–55]. For example, cyclohexanone oxime, which is a key intermediate for manufacturing  $\epsilon$ -caprolactam, is conventionally prepared via the hydroxylamine oxidation route, including hydroxylamine sulfate oxidation (HSO) and hydroxylamine phosphoric oxidation (HPO) approaches [56, 57]. Generally, it involves many harsh drawbacks in these approaches, i.e., long and complex reaction pathways, high energy and material consumed, generating a large amount of waste and side-products, and harmful for health and environment, as shown in **Scheme 2**. To overcome these drawbacks, a “one-step” cyclohexanone ammoximation process with  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$  was developed by EniChem in 1986 using TS-1 as a catalyst under very moderate conditions [58, 59]. Compared with traditional route, the novel one is highly clean and environmental friendly, with evidently reducing of waste production and capital cost, only water as a side product. The first 12 Kt/a demonstration unit with TS-1 catalyst had been built up by EniChem in 1994, and a commercial 60 Kt/a unit was carried out by Sumitomo in 2003. By using HTS as a catalyst, a 140 Kt/a commercial cyclohexanone

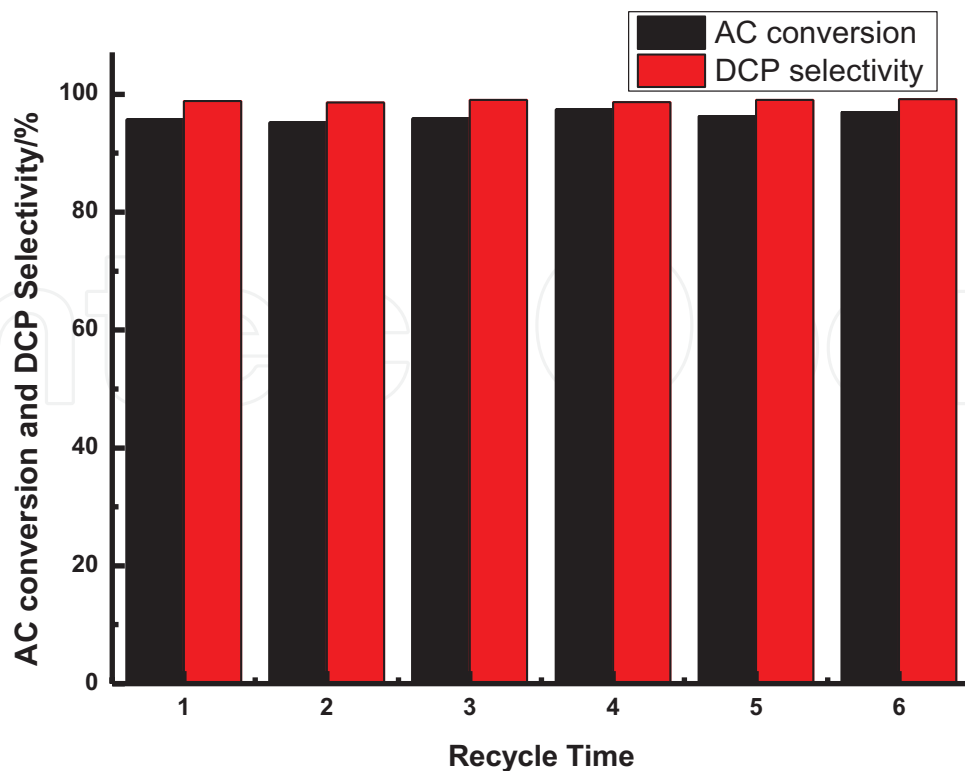
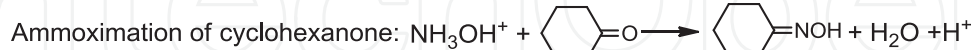
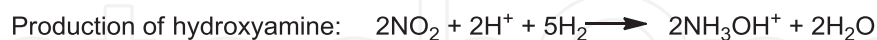


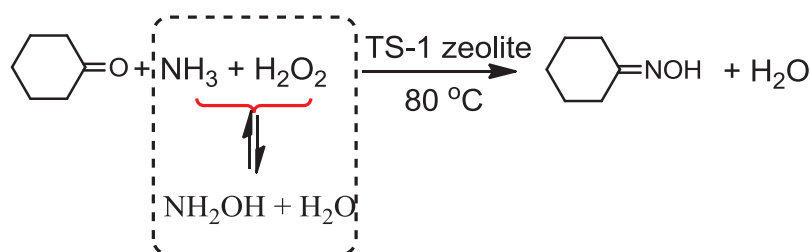
Figure 6. Conversion of AC and DCP selectivity in the reuse experiments six times under the same reaction conditions.

ammoximation process was built by SINOPEC, and it run smoothly for over 10 years since 2000 [60]. Similar to this process, acetone ammoximation with  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$  catalyzed by HTS also carried out, with high acetone conversion and oxime selectivity [61].

(a) *Traditional "four-steps" method*



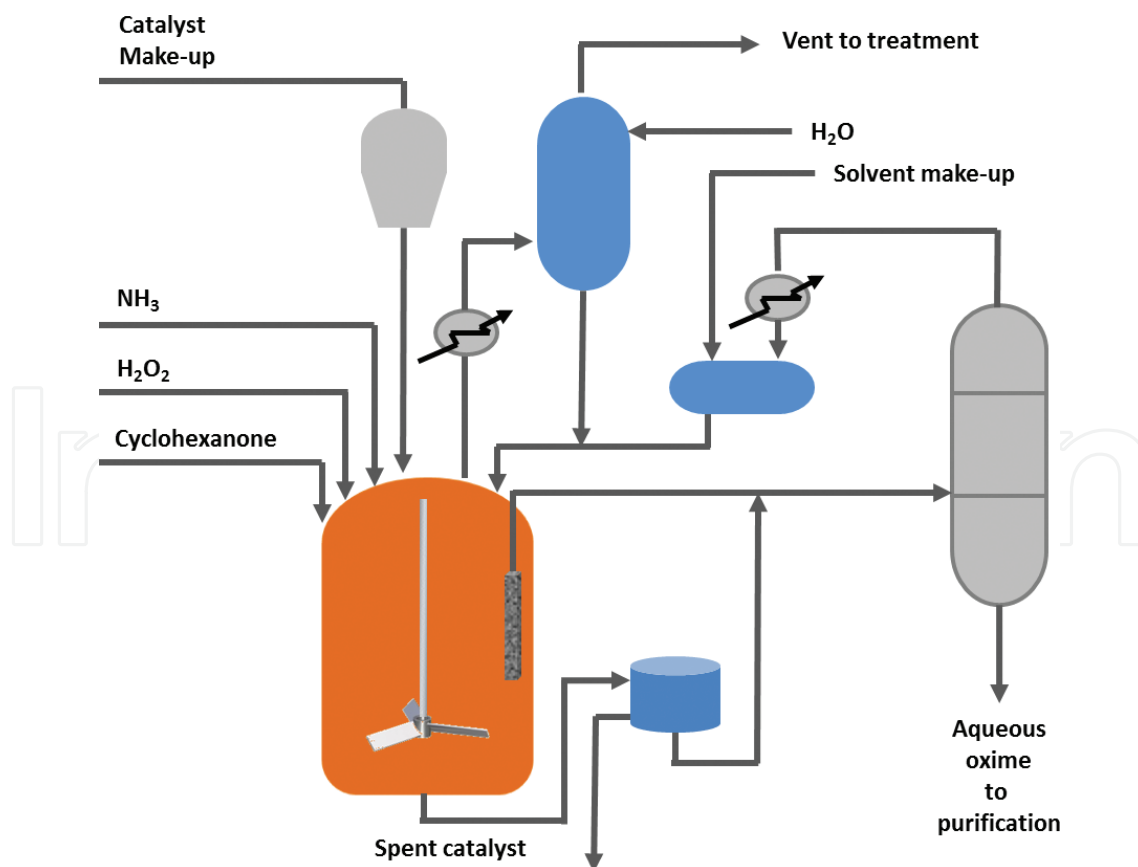
(b) *"One-step" method*



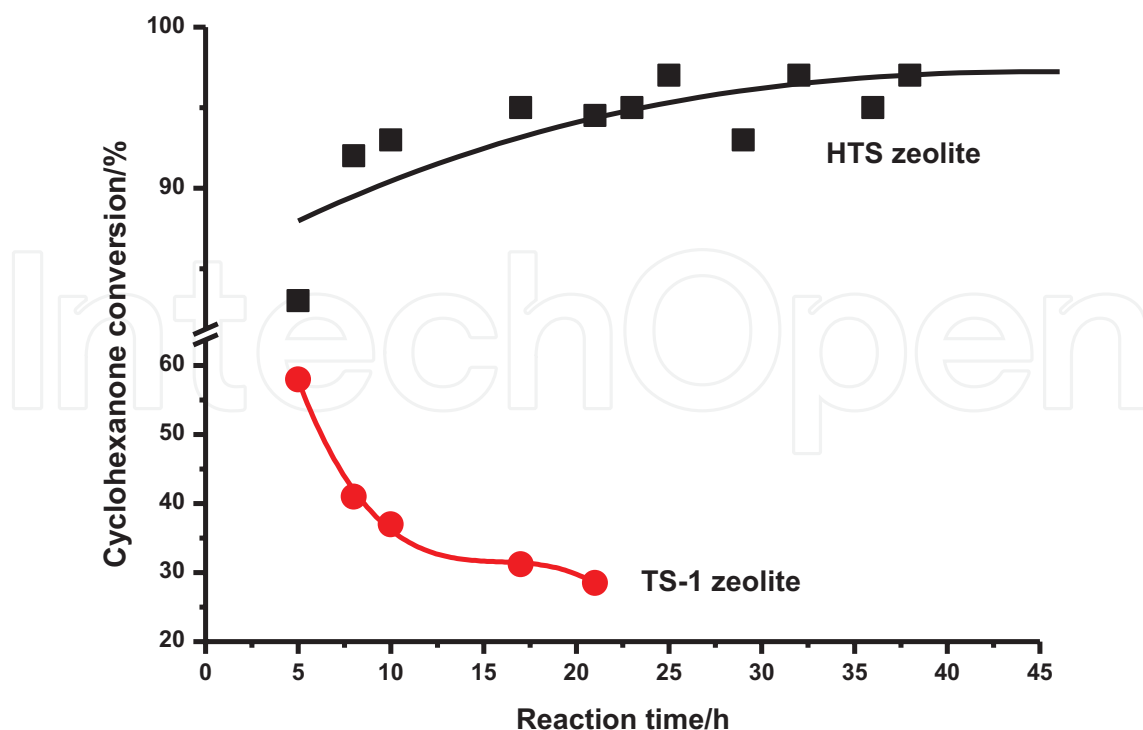
Scheme 2. Comparison of traditional HSO (HPO) route and novel TS-1 catalyzed ammoximation reaction for the production of cyclohexanone oxime.

The mechanism of “one-pot” cyclohexanone ammoximation bases on the *in-situ* formation of hydroxylamine ( $\text{NH}_2\text{OH}$ ) through the oxidation of  $\text{NH}_3$  with  $\text{H}_2\text{O}_2$  under the effect of tetrahedral Ti species, and then it reacts with cyclohexanone to form oxime [62, 63]. The coordination of  $\text{NH}_3$  and  $\text{H}_2\text{O}_2$  with framework Ti sites has been investigated by a spectroscopic method, perfectly with an octahedral coordination. And the cyclohexanone ammoximation reaction was operated in a stirred reactor through a continuous liquid phase flow, with a slurry medium (TS-1 catalyst concentration is about 2–3 wt%) at 80–90°C. It is noted that the TS-1 and HTS zeolite particles are about 300–500 nm in size, which are too small to be separated by conventional methods and equipment. Thus, the separation of catalyst from reaction mixture and solvent (*tert*-butanol) is usually carried out in a membrane filter, and then crude oxime is withdrawn from the bottom of this reactor for further purification, and the spent catalyst should be separated from this reaction system and calcined to remove the organic deposit, which fills the channel of TS-1 zeolite, as shown in **Figure 7**.

As shown in **Figure 8**, we can see that HTS zeolite is of far higher catalytic performance and longer lifetime than TS-1 under the same conditions. This is because hollow cavities well enhance the mass diffusion within zeolite particles, and relative short residence time of cyclohexanone favors the decrease of side products, especially for heavy organic deposits. Moreover, the ultrahigh stability of HTS is attributed to the recrystallization of zeolite defects



**Figure 7.** Diagrammatic sketch of a “one-step” cyclohexanone ammoximation process catalyzed by TS-1 zeolite under moderate conditions.



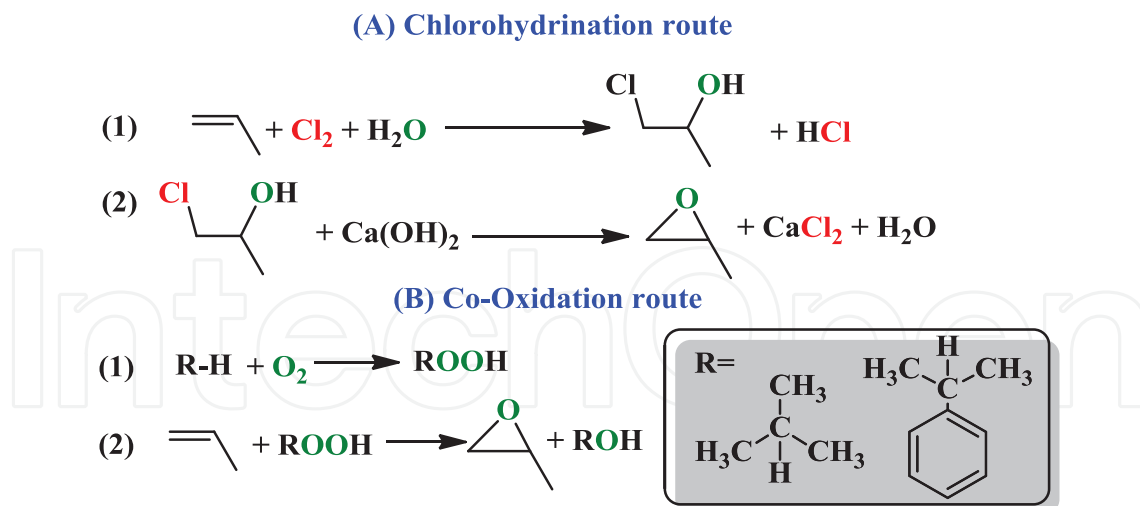
**Figure 8.** Comparison of catalytic performance of HTS and TS-1 zeolites in the cyclohexanone ammoximation process with  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$ .

through dehydrated condensation between Si-OH and Ti-OH groups, making it more tolerant to alkaline intermediates.

In addition, in our previous works, the irreversible deactivation of HTS zeolite has been investigated by using multiple characterization methods and catalytic evaluations [64–66]. It is confirmed that the dissolution of framework Si atoms and the removal of framework Ti atoms cause the formation of acidic amorphous  $\text{TiO}_2\text{-SiO}_2$  nanoparticles, leading to the inefficient decomposition of  $\text{H}_2\text{O}_2$  molecules during catalytic oxidation processes. At the same time, the simulated deactivation of HTS in aqueous  $\text{NH}_3$  solution was also examined, and finally, an efficient and easy regeneration method has been developed.

## 6. Epoxidation of olefins with $\text{H}_2\text{O}_2$

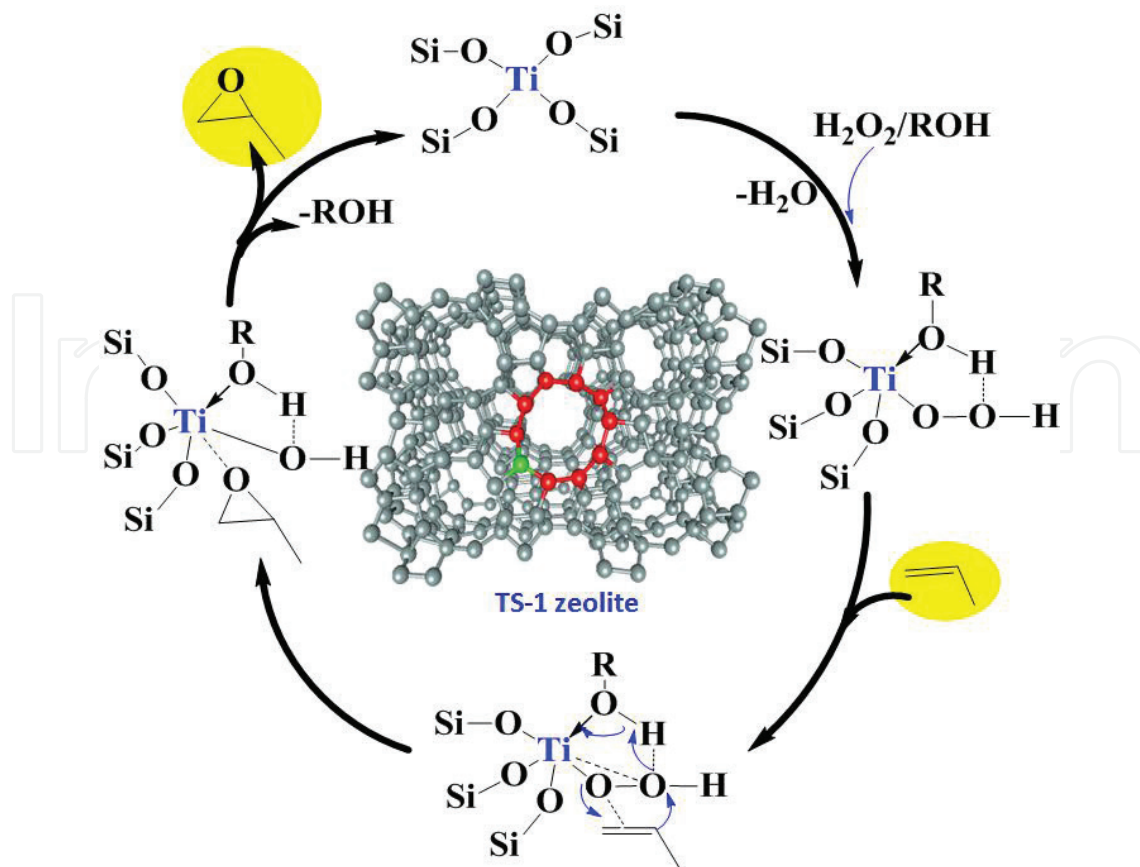
Olefin epoxidation with  $\text{H}_2\text{O}_2$  to prepare epoxy compound is an ultrakey reaction for manufacturing chemical intermediates, which is highly relevant with all aspects of human life and social production [67–69]. Particularly, propylene oxide (PO), one of the three large propylene derivatives, is majorly produced via a combined chlorohydration-saponification technology and a cooxidation method in traditional route, as shown in **Scheme 3**. Chlorohydration route lines in the oxidative addition of propylene with  $\text{Cl}_2$  and  $\text{H}_2\text{O}$  to give birth to chloropropanol and HCl, and then chloropropanol reacts with  $\text{Ca}(\text{OH})_2$ , with the formation of propylene oxide. We can conclude that the O atom in PO molecule comes from the  $\text{H}_2\text{O}$  molecule, and a large amount of hazardous by-products and wastewater are caused by  $\text{Cl}_2$  and  $\text{Ca}(\text{OH})_2$  [70–72]. As a result, a much greener PO manufacture technology catalyzed on TS-1 (remarked



**Scheme 3.** Reaction networks of chlorohydration route and cooxidation route for the production of propylene oxide in industry.

as HPPO) was exploited by EniChem, and then several commercial HPPO units based on TS-1 catalysts were built up and run smoothly in around 2010, significantly reducing the generation of wastewater and unwanted products [73, 74].

**Scheme 4** presents the reaction pathways of epoxidation of propylene with  $\text{H}_2\text{O}_2$  under the impact of tetrahedral Ti species, while the five-member ring (originated from framework



**Scheme 4.** Reaction mechanism of propylene epoxidation with  $\text{H}_2\text{O}_2$  catalyzed by TS-1 zeolite.

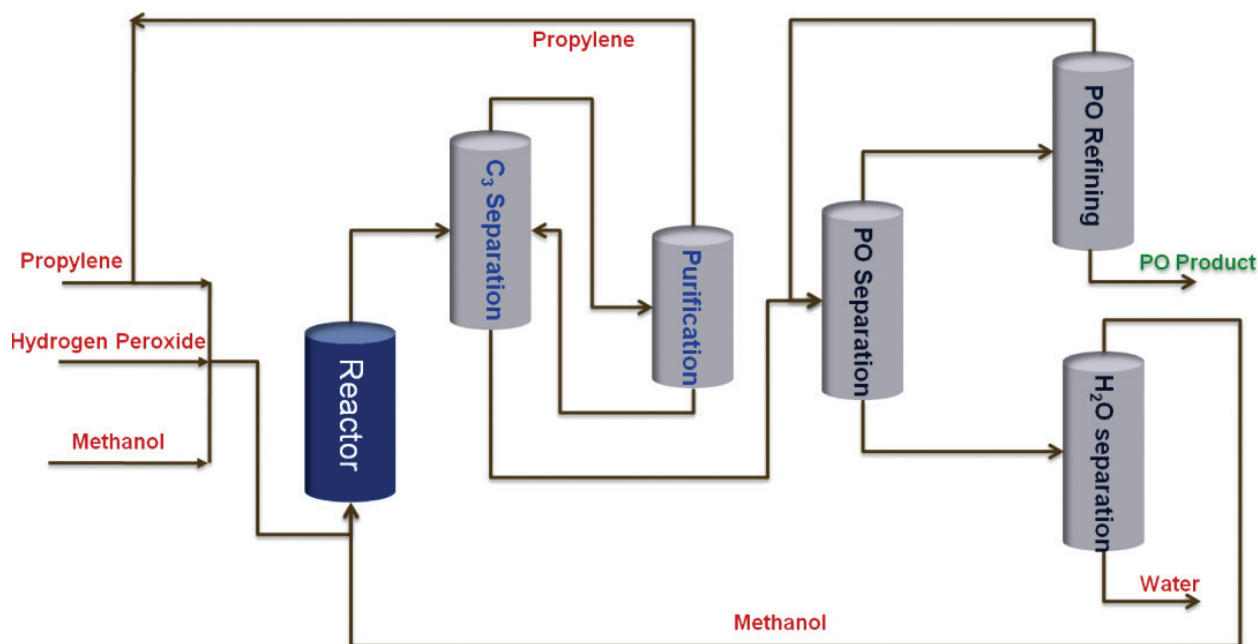


Figure 9. Diagrammatic sketch of propylene epoxidation with  $\text{H}_2\text{O}_2$  catalyzed by HTS zeolite.

Ti site, solvent, and  $\text{H}_2\text{O}_2$ ) mechanism is well accepted, as shown in **Scheme 4**. To verify this mechanism, many characterization and calculation methods were employed and summarized. Since 2000, HTS zeolite was also applied in the HPPO process, showing extreme high catalytic performance and stability. Moreover, the commercial 100 kt/a HPPO unit had been established and run well for over 6000 h, based on the promising result of pilot unit (at a 10 kt/a scale), as illustrated in **Figure 9**. The demonstration process of HPPO catalyzed by HTS was carried out in a fixed-bed reactor under mild conditions, with over 97%  $\text{H}_2\text{O}_2$  conversion and 96–99% PO selectivity at the same time, as shown in **Figure 10**. It is even higher than that

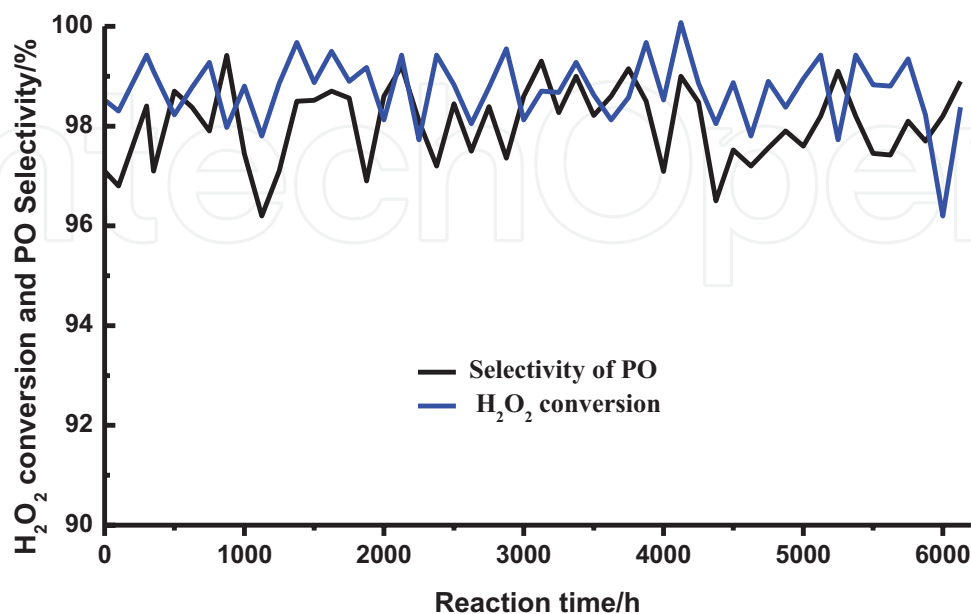


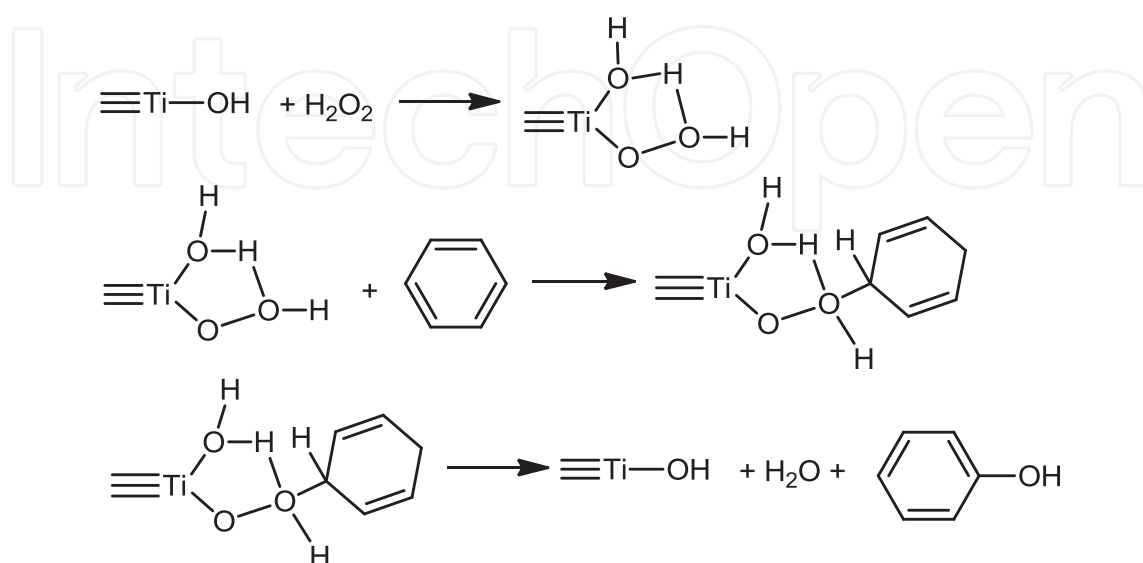
Figure 10. Catalytic performance of HTS zeolite in propylene epoxidation at pilot scale.

reported by BASF and DOW (the selectivity of PO is about 93.2%), attributing to the benefits of intracrystalline mesopores [75].

In addition, after the purification of crude PO in a distillation column, the final PO product has a high purity of 99.97%, which had already been used as chemical intermediates to manufacture 1,2-ethyl glycerol, oilfield demulsifier, propylene carbonate, triisopropanolamine, hydroxypropyl, dimethyl carbonate in market. Up to date, one even larger scaled (300 kt/a) industrial HPPO demonstration unit is under constructing, based on the previous experiment results [76].

## 7. Hydroxylation of aromatics with H<sub>2</sub>O<sub>2</sub>

Green hydroxylation of aromatics to phenolic derivatives, such as phenol, cresol, catechol, and hydroquinone, is still a huge challenge for producing many kinds of fine chemicals in industry, due to the strong charge delocalization effect of six-member ring of benzene [77–79]. The production of phenol is mainly on the basis of the commercial cumene process, which contains a three-step process (that is alkylation of benzene with propylene, cumene oxidation, and acid-catalyzed decomposition), with acetone as the major by-product. As acetone is very cheap and superfluous than its consumption, this process is suffered by the capital cost and acetone market. Moreover, this route has a very complex and long pathway, and gives birth to a large amount of by-products due to the severe reaction conditions. As a result, several selective catalysts were proposed, such as V, Fe, and Cu-based catalysts, but they are far beyond to be used in a large scale due to their poor catalytic activity or stability. Direct benzene oxidation to phenol with H<sub>2</sub>O<sub>2</sub> catalyzed by TS-1 is widely accepted as an alternative process to the traditional cumene process for producing phenol, as shown in **Scheme 5**. As previously mentioned, the function of TS-1 catalyst involves the activation of H<sub>2</sub>O<sub>2</sub> oxidant to form a highly reactive Ti-OOH species, which can easily nucleophilic attack the C atoms in



**Scheme 5.** Mechanism of benzene hydroxylation with H<sub>2</sub>O<sub>2</sub> catalyzed by TS-1 zeolite.



benzene molecules. Moreover, TS-1 zeolite is ultrastable and can be even used in the strong acid media. Some other metal-incorporated zeolites, such as Ti-beta, Ti-MOR, and V-beta, were also evaluated by direct benzene oxidation, but they were of lower catalytic performance than TS-1.

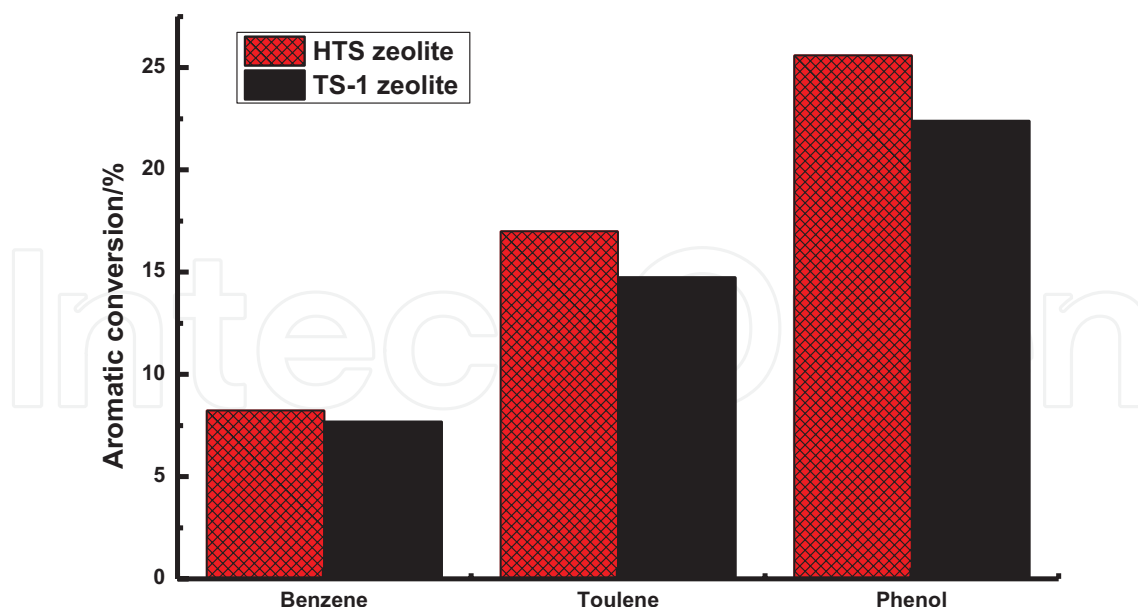
Furthermore, phenol hydroxylation to produce catechol and hydroquinone is also of great importance for fine chemical production, such as agrichemical, photography chemicals, anti-oxidants, polymerization inhibitors, etc [80, 81]. In conventional routes, the dihydroxybenzenes are commercially produced by several complex processes, including (i) the oxidations of aniline and diisopropylbenzene and (ii) sulfurization of benzene and hydrolysis of benzene sulfonate [82]. **Table 2** shows the detailed technologies for the production of dihydroxybenzenes in industry, but some of them have been sifted out, owing to inevitable limitations. We can see that HTS zeolite demonstrates the highest catalytic performance and technical advantages among these catalysts, especially when taking the environmental and cost benefits into consideration. It was developed and commercially scaled up by EniChem in 1986 for the first time to substitute the Brichima process, avoiding the separation problem of homogeneous catalyst.

After 2000, phenol hydroxylation catalyzed by HTS zeolite was established, with significant reduction of financial investment and operation cost. It is worthy to note that the catalytic activity of TS-1 zeolite in this reaction is closely associated with the chemical status of Ti species; only tetrahedral framework Ti species are able to promote the activation of  $H_2O_2$  oxidant, rather than the substrate. Therefore, phenol hydroxylation is usually chosen as a probe reaction to reveal the intrinsic activity of framework Ti sites incorporated.

Additionally, to illustrate the preponderance of hierarchical structure, both TS-1 and HTS zeolites were evaluated by several aromatic (including benzene, toluene and phenol) oxidation reactions, as shown in **Figure 11**. It is observed that HTS zeolite exhibits much higher catalytic performance than TS-1 zeolite in all aromatic oxidation we tested, with ultralong lifetime in these reactions as well. This ascribes to the higher content of framework Ti species of HTS than TS-1, and the improvement of mass diffusion via the formation of hollow cavities, which is in great agreement with the dissolution-recrystallization process through post-synthesis treatment. Accordingly, these results suggest that phenol molecules are more active than toluene, and far more reactive than benzene, in TS-1 catalyzed aromatic oxidations, due to the change of charge property by introducing electronic groups. It is interesting to find that the solvent effect takes great impact on the catalytic performance of TS-1 zeolite, while acetic acid can promisingly enhance toluene conversion in the presence of  $H^+$  ions.

Approach	Catalyst	$X_{\text{phenol}}$ (%)	$S_{\text{p- and o-product}}$ (%)
Rhone-Poulenc	$H_3PO_4/HClO_4$	5	90
Ube	Ketone peroxide/ $H_2SO_4$	<5	90
Brichima	Fe(II)/Co(II)	10	80
EniChem* ( $H_2O_2$ /phenol = 1/3)	HTS	26	>95

**Table 2.** Different phenol hydroxylation approaches to produce catechol and hydroquinone.



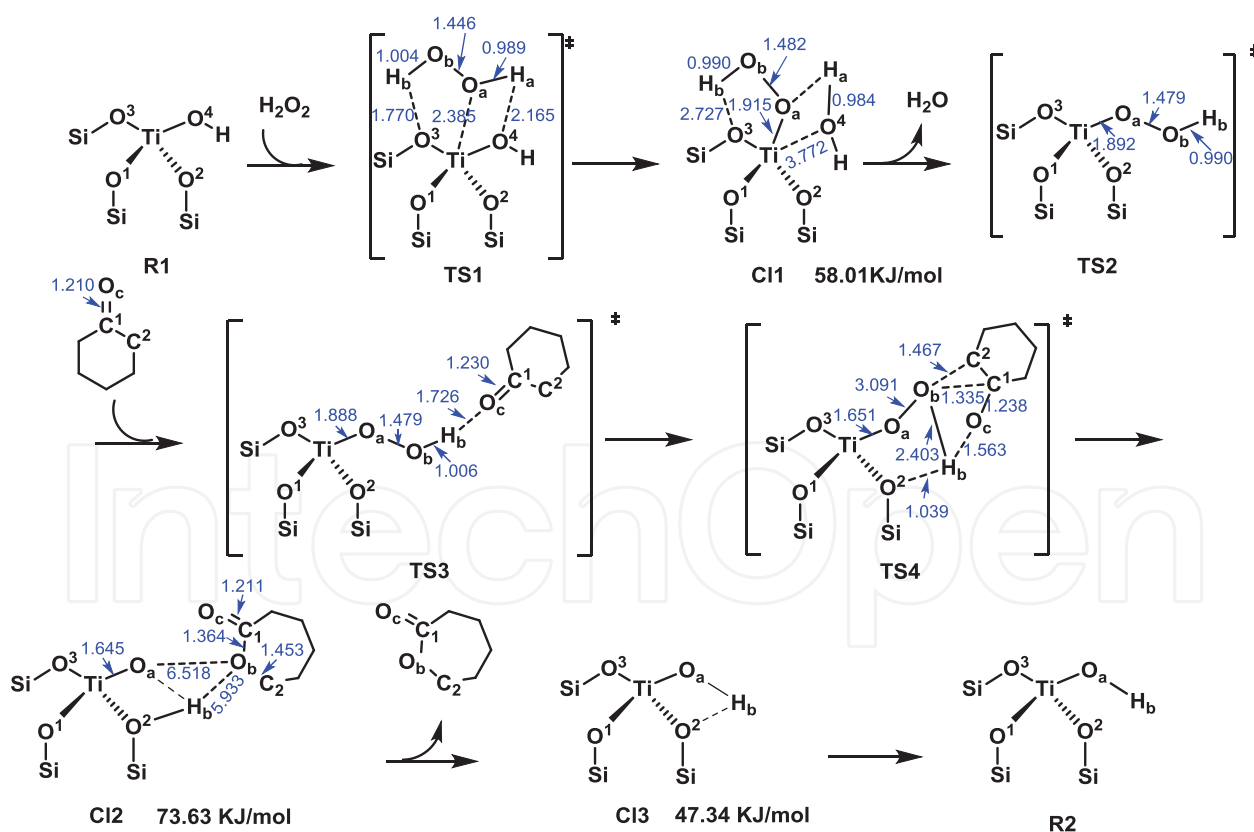
**Figure 11.** Catalytic performance of TS-1 and HTS in various aromatic oxidation with  $\text{H}_2\text{O}_2$ , reaction conditions: (A) benzene/ $\text{H}_2\text{O}_2 = 1:1$ , solvent free,  $70^\circ\text{C}$ , 400 rpm; (B) toluene/ $\text{H}_2\text{O}_2 = 1:1$ , acetic acid as solvent,  $70^\circ\text{C}$ , 400 rpm; (C) phenol/ $\text{H}_2\text{O}_2 = 3:1$ , acetone as solvent,  $80^\circ\text{C}$ , 400 rpm.

Generally, the ratio of catechol to hydroquinone is close to 1:1 in the TS-1 catalyzed phenol hydroxylation route, and catechol (para-dihydroxybenzene) is more expansive and of even larger requirement than the other one. Recently, we have proposed an efficient route to modify the product distribution, with obviously increasing of para-product selectivity, by introducing acidic-basic sites via adding  $\text{MgO-Al}_2\text{O}_3$  binary oxides. For  $\text{MgO-Al}_2\text{O}_3$  modified HTS zeolite [83], the optimized ratio of para to ortho product is larger than 2, while the phenol conversion still remains high (>16%). The high *p*-dihydroxybenzene selectivity is ascribed to the steric hindrance and the synergistic effect between Lewis basic-acidic sites of mixed oxides and tetrahedral framework Ti species in HTS zeolite. In other words, HTS zeolite provides an ideal platform to transform aromatics into phenolic derivatives under mild conditions, to make these processes gradually be much cleaner and greener.

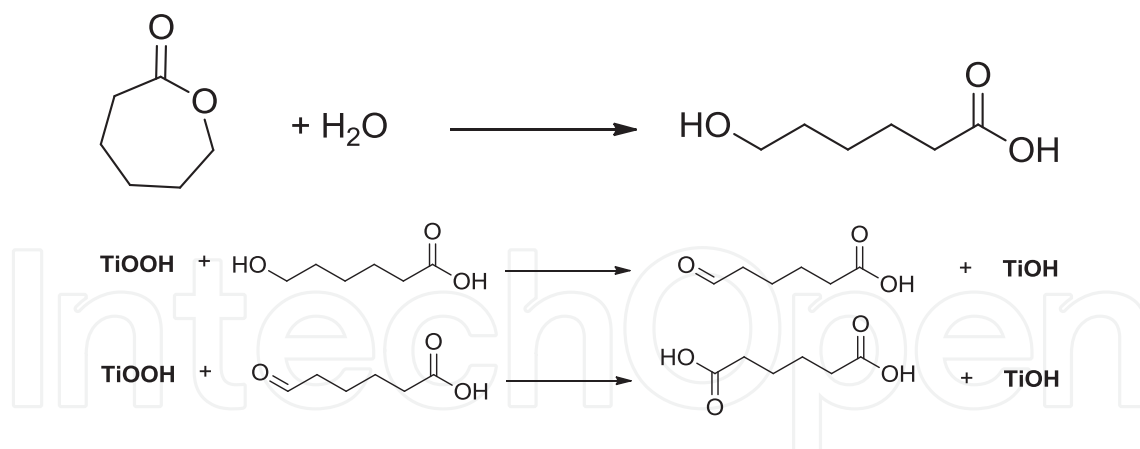
## 8. Baeyer-Villiger oxidation of cyclohexanone with $\text{H}_2\text{O}_2$

Baeyer-Villiger (BV) oxidation is of great importance to convert ketones to esters or lactones, which are important organic intermediates in the fine chemical industry [84–90].  $\epsilon$ -caprolactone is traditionally produced from the BV oxidation reaction of cyclohexanone by using peracids as a catalyst and oxidant, e.g., perbenzoic acid, *m*-chloroperbenzoic acid, and trifluoroperacetic acid. Although peracids route favors high ketone conversion and fast product transformation, it suffers serious pollution and operation drawbacks at commercial scale [91–97]. Aqueous hydrogen peroxide solutions (usually with 30–50 wt% concentration), environmental friendly, cheap, and easy to handle, are considered as a desirable oxidant to replace hazardous peracids. However, hydrogen peroxide is usually of less attacking nucleophilic capability than peracids for activating the carbonyl group of ketones [98–102].

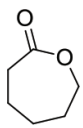
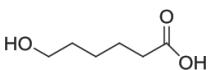
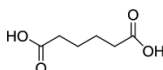
In previous works, much effort has been devoted to develop both homogeneous and heterogeneous catalysts in order to improve the performance of BV oxidation of cyclohexanone [104–111]. One famous catalyst is Sn-beta zeolite, reported by A. Corma, with almost 100%  $\epsilon$ -caprolactone selectivity in direct BV oxidation of cyclohexanone in organic solvent at low temperature ( $<90^\circ\text{C}$ ) [112]. It is confirmed that this route bases on the activation of carbonyl group by tetrahedral framework Sn species via the acceptor-donor of electron pairs between framework Sn sites and O atoms in cyclohexanone. In contrast, we have found that HTS zeolite is also an effective catalyst for the BV oxidation of cyclohexanone with  $\text{H}_2\text{O}_2$ , but further hydrolysis and oxidation of lactone have been occurred with the formation of 6-hydroxyhexanoic acid and adipic acid, respectively. As for the mechanism of this reaction, the density function theory (DFT) method was employed, which suggests that the activation of  $\text{H}_2\text{O}_2$  to form highly reactive Ti-OOH species is the driving force of BV oxidation, as shown in **Figure 12**. However, due to its seven-member-ring structure,  $\epsilon$ -caprolactone easily reacts with  $\text{H}_2\text{O}$  to make ring-opening reaction occurred with the formation of 6-hydroxyhexanoic acid. Then, the hydroxyl-substituted acid will further be oxidized by Ti-OOH species, to give birth to adipic acid in the end, as shown in **Figure 13**. To support our proposed mechanism, the major products of cyclohexanone BV oxidation were analyzed by the gas chromatography-mass spectrometry method,



**Figure 12.** One possible reaction pathway of cyclohexanone BV oxidation catalyzed by TS-1 zeolite involving the activation of  $\text{H}_2\text{O}_2$  molecules [103].



**Figure 13.** Reaction network of ring opening of ε-carprolactone and deep oxidation of 6-hydroxyhexanoic acid to adipic acid.

Catalyst	Reaction condition			Conversion (%)	Target product selectivity (%)		
	Solvent	Temp. (°C)	Time (h)		 ε-Carprolactone	 6-Hydroxyhexanoic acid	 Adipic acid
HTS	–	90	8	59.51	0.75	61.21	28.52
Sn-beta	MTBE/ dioxane	90	3	52	>98	–	–

**Table 3.** Reaction parameters and catalytic performance of Sn-beta and HTS in the cyclohexanone BV oxidation with H<sub>2</sub>O<sub>2</sub>.

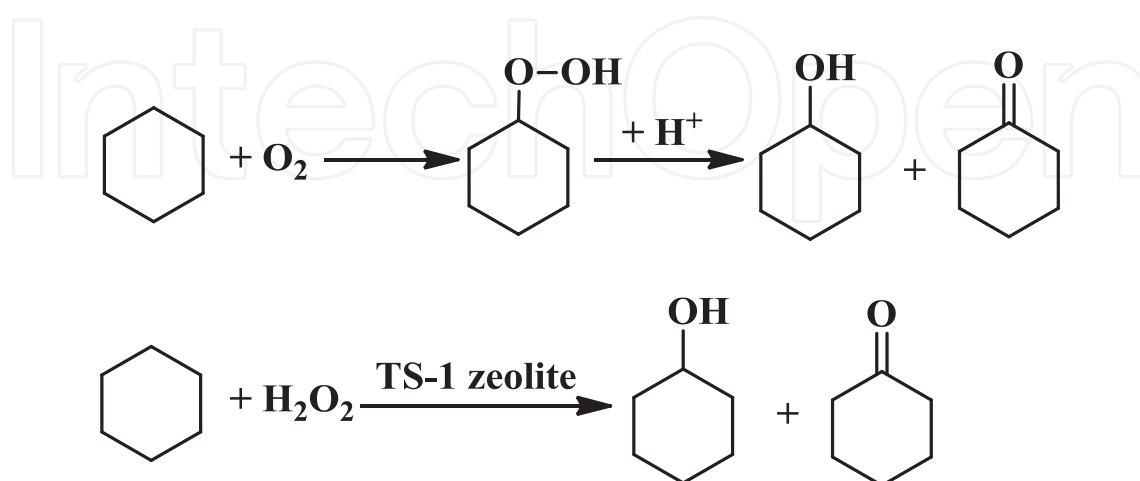
including 6-hydroxyhexanoic acid, adipic acid, cyclohexane-diol, and cyclohexane-dione. As shown in **Table 3**, HTS zeolite has a much higher conversion (with longer reaction time) than Sn-beta zeolite, without adding any organic solvent. And we also observe that increasing reaction temperature and H<sub>2</sub>O content are in favor of high cyclohexanone conversion and acid yield. It is in good agreement with the DFT result which indicated that the framework Ti species display a totally novel catalytic behavior from that Sn species incorporated, attributing to the basic difference of charge property between them.

From the viewpoint of commercial application, although ε-carprolactone selectivity in HTS catalyzed route is far lower, it provides an ideal and green approach to produce adipic acid, overcoming the significant drawbacks of oxidation of KA oil with HNO<sub>3</sub>, and there is no organic solvent added, reducing the energy consumption for solvent recycling and purification. Most importantly, the product distribution can be altered, according to market requirement, via changing reaction parameters and processing technologies.

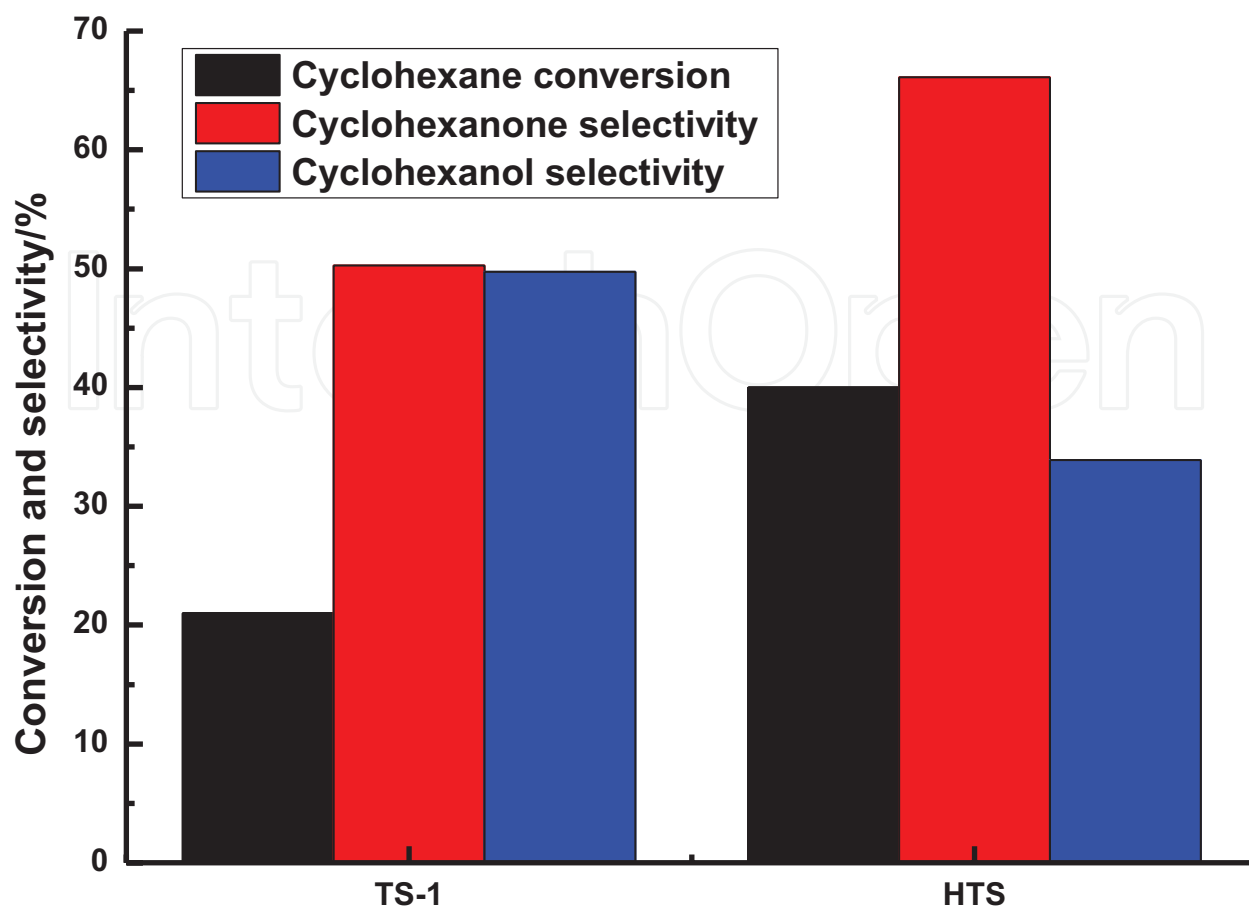
## 9. Catalytic oxidation of cyclohexane with $\text{H}_2\text{O}_2$ to KA oil

Cyclohexane oxidation to prepare cyclohexanone and cyclohexanol (referred as to KA oil) is always a hot spot in the organic chemical industry, contributing to the wide application area of KA oil [113–115]. Currently, KA oil is mainly manufactured by the air oxidation of cyclohexane via the formation and decomposition of cyclohexyl peroxide at over  $100^\circ\text{C}$  in industry, using soluble cobalt carboxylate and metal-boric acid as a catalyst, or without a catalyst, with about 80% selectivity of KA oil, as shown in **Scheme 6**. However, the cyclohexane conversion should be kept at ultralow level, about 4–10% for single transformation, to reducing the selectivity of undesired products, such as adipic acid and deep hydroxylated products. Apart from the harsh reaction parameters, homogeneous catalysts are usually difficult to be separated from mixture, with high power consumption. During the past centuries, huge efforts on developing benign oxidation of cyclohexane with various oxidants (including  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , and *tert*-butyl hydroperoxide (TBHP) and catalysts have been devoted. Among them, HTS zeolite exhibits delightful catalytic performance, with  $\text{H}_2\text{O}_2$  as an oxidant under mild conditions, as shown in **Figure 14**. It is apparent to illustrate that the cyclohexane conversion for HTS zeolite is as twice the time as that of TS-1 in the same reaction conditions, owing to the intensification of the accessibility of framework Ti species through hollow cavities. Except for the excellent conversion rate, HTS zeolite is also helpful for the high selectivity of cyclohexanone, by promoting the further oxidation of cyclohexanol with  $\text{H}_2\text{O}_2$ .

Particularly, it should be mentioned that the selectivity of KA oil is much higher than that of air-oxidation route, over 90% under optimized conditions. Although  $\text{H}_2\text{O}_2$  solution is much more expensive than air, there is no need to carry out the complex separation and only few by-products formed, with higher atom utilization efficiency and thus meeting the principles of green chemistry. Consequently, this route provides an alternative method for KA oil production to replace the conventional route, and the scale up study is still under investigating



**Scheme 6.** Comparison of cyclohexane oxidation reaction network between commercial route and TS-1 catalyzed route with  $\text{H}_2\text{O}_2$ .



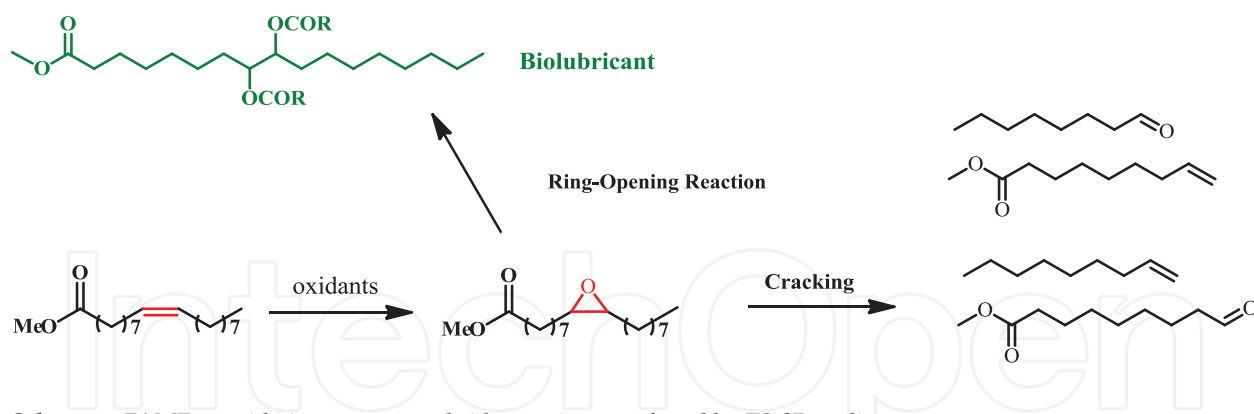
**Figure 14.** Catalytic performance of TS-1 and HTS in cyclohexane oxidation with  $H_2O_2$  (reaction conditions:  $H_2O_2$ /cyclohexane = 1:1, 5 wt% catalyst content, 80°C, 500 rpm stirring).

at SINOPEC. We confirm that it is of great industrial potential, when taking the successful commercialization cases into consideration.

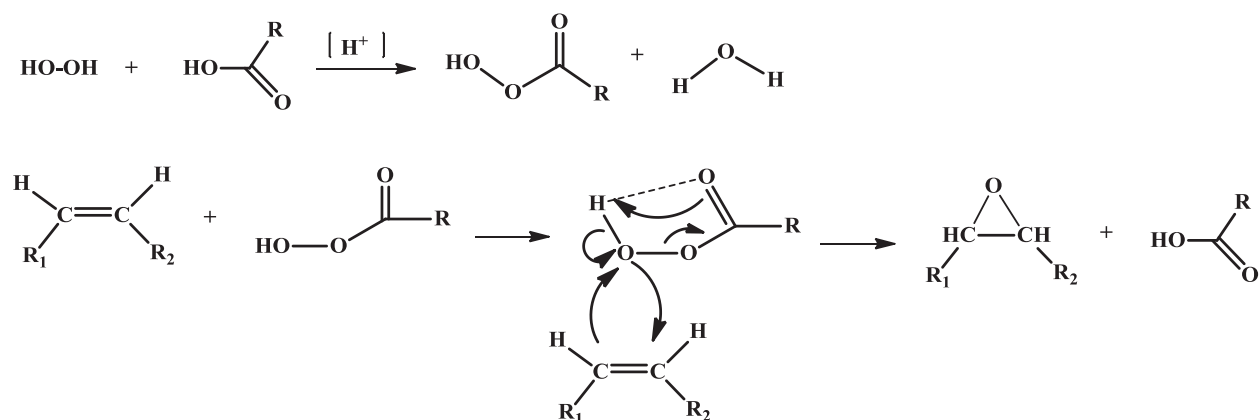
## 10. Epoxidation of fatty acid methyl ester with TBHP

As the fast developing of transformation of biomass to bulk and fine chemicals, green conversion processes for biomass utilization become particularly important [116–118]. In this context, epoxy fatty acid ester, one of the largest-scale chemicals derived from biodiesel, has been widely used as environment-friendly polyvinyl chloride (PVC) plasticizer and intermediates in the production of fine chemicals, such as nonanal, nonene, and other bulky molecules used as a biolubricant. In industry, epoxy fatty acid ester is adopted by the peracid process (Prileshajev reaction, **Schemes 7** and **8**). However, the Prileshajev method is of low efficiency, high risk, and pollution, due to the use of inorganic acid as catalyst and hazardous peracids as an oxidant.

Recently, we have developed a heterogeneous FAME epoxidation process with TBHP catalyzed by titanosilicate zeolite to replace the Prilezhaev method. While due to mass transfer



Scheme 7. FAME epoxidation process and side reactions catalyzed by TS-SP zeolite.



Scheme 8. Reaction pathways of the Prilezhaev reaction with  $\text{H}_2\text{O}_2$  in industry.

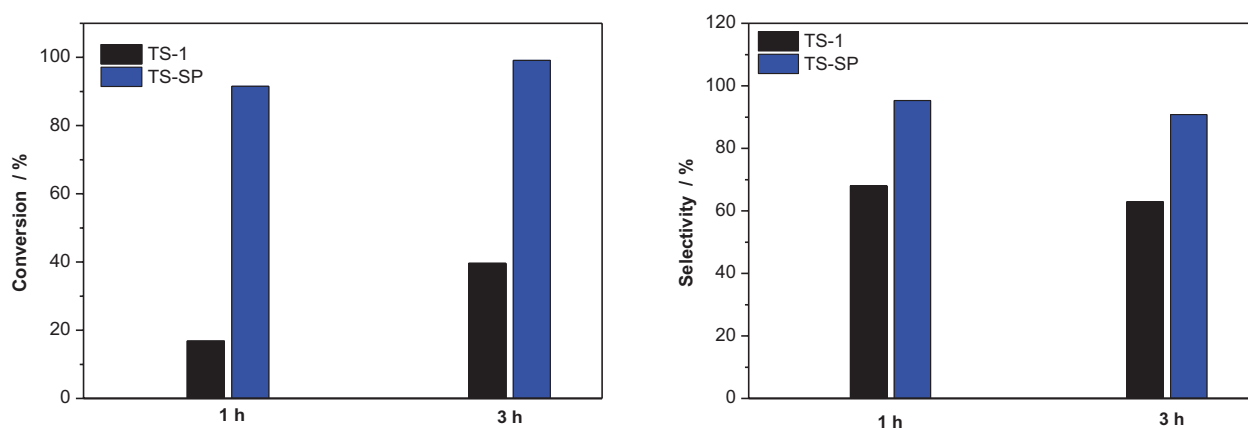
limitation of FAME, TS-1 presents low activity with FAME conversion of 16.8% and a fairly low epoxy fatty acid ester at 0.5 h. In order to overcome mass transfer limitation in TS-1, several methods have been proposed. Recently, we have exploited a hierarchical titanosilicate zeolite with spongy structure (TS-SP) by combining pore-embedding and post-treatment methods. The specific surface area of TS-SP calculated by Brunauer-Emmett-Teller (BET) method (Table 4) is  $518 \text{ m}^2\cdot\text{g}^{-1}$ , comparing with TS-1 of  $435 \text{ m}^2\cdot\text{g}^{-1}$ , corresponding external surface area calculated by the t-plot method is  $342 \text{ m}^2\cdot\text{g}^{-1}$ , which is also far more than traditional TS-1, indicating the existing of mesopores or macropores. Pore-size distribution and cumulative pore volume calculated by a nonlocal density functional theory (NL-DFT) model confirmed that obvious and abundant mesopores distributed in the range of 3–5 nm were formed in the zeolite. Thus, in epoxidation of FAME, the uniform mesopores promote the diffusion

Zeolites	Ti/Si ratio (%)	$S_{\text{BET}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$S_{\text{ext}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3\cdot\text{g}^{-1}$ )	$D_{\text{meso}}$ (nm)
TS-1	3.58	435	8	0.181	2.5, 4.3
TS-SP	3.51	518	342	0.077	3–5.5

Table 4. Textural parameters and elementary composition of titanosilicate zeolites.

of FAME and TBHP molecules inside the zeolites, leading to the better accessibility of active sites and facilitating product transport outside the pores, as shown in **Figure 15**. As a result, the spongy zeolite shows even more remarkable catalytic activity with 91.5% conversion at 0.5 h, which is 5.4 times as that of TS-1. What is more, FAME could be completely consumed within only 3 h, with the epoxy product selectivity more than 90%, which is far higher than that of TS-1. To the best of our best knowledge, this result is close to the highest performance published in the literature so far.

In conclusion, heterogeneous catalytic epoxidation of FAME is of significant importance for the environmental protection, saving energy, and improving selectivity of target product, as it avoids the use of hazardous peracids and inorganic acids. Those achievements confirm that mass transformation limitation of FAME could be solved by introducing hierarchical pores with zeolite particles, bringing significant enhancement of catalytic activity in bulk molecule oxidation reactions.



**Figure 15.** Catalytic performance of various TS-1 zeolites in epoxidation of methyl oleate with TBHP.

## 11. Conclusion and perspective

In summary, we have systematically reviewed the synthesis of hierarchical TS-1 zeolites and their catalytic application in several oxidation processes at SINOPEC, to replace the hazard and polluted traditional routes. In the early years, HTS zeolite was synthesized by using a “dissolution-recrystallization” treatment under hydrothermal conditions, which demonstrates much higher catalytic performance than conventional TS-1 zeolite, due to the diffusion improvement by intracrystalline confined mesopores. In addition, post-synthesis helps the reincorporation of Ti species into the framework matrix, thus HTS zeolite exhibits excellent activity in many commercial processes, such as propylene epoxidation, cyclohexanone ammoximation, and phenol hydroxylation. Moreover, we have already developed several interesting oxidations, such as chlorohydrination of AC with  $H_2O_2$  and HCl and cyclohexanone BV oxidation with  $H_2O_2$ , for meeting the requirements of sustainable and green chemistry. On



the other side, we also paid more attention on the exploitation of hierarchical TS-1 zeolites, for enhancing the entrance and mass diffusion with open mesopores, by using combined silanization and post-treatment technologies. Therefore, the application of TS-1 zeolites has been extended to the catalytic oxidation of bulk substrates and oxidants (TBHP and CHHP), showing far better advantages in the epoxidation of FAME with TBHP over the Prileshajev reaction with  $H_2O_2$ . Most importantly, after long-term experiment and thinking, we can rationally design and synthesize hierarchical TS-1 zeolites with different kinds of mesopores at molecular scale, according to the demands for specific reactions. Furthermore, these catalytic materials provide bright opportunities for replacing traditionally polluted oxidation processes, and many successful cases have been achieved. For further development, many novel hierarchical zeolites with different framework composition and new topological structures will be prepared, and then these materials will also find many cleaner catalytic reactions, with an evident of reducing the generation of waste and unwanted products.

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