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Hollow Titanium Silicalite Zeolite: From Fundamental Research to Commercial Application in Environmental-Friendly Catalytic Oxidation Processes

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Abstract

The systematical investigation on the synthesis, characterization, formation mechanism, and catalytic application of hollow titanium silicalite (HTS) zeolite has been reviewed. HTS is prepared through a “dissolution–recrystallization” post-treatment in the presence of template under hydrothermal conditions. Compared with TS-1, HTS is of unique hollow voids and with high framework Ti content, which significantly increase the mass diffusion and the amount of active sites, respectively. Thus, HTS zeolite displays high catalytic activity and stability in many oxidation processes with H_2O_2 oxidant, that is, cyclohexanone ammoximation, phenol hydroxylation, propylene epoxidation, Baeyer-Villiger oxidation of cyclohexanone, and selective oxidation of aromatics and cycloalkanes. The former three ones have been commercialized and run smoothly, which have promising economic and environmental significance.

Keywords: Hollow Titanium Silicate, Environmental friendly, Post synthesis, Selective oxidation, Commercialization

1. Introduction

Zeolites are regular microporous materials composed by TO_4 tetrahedra (T stands for Al, Si, Sn, Ti, and B) through sharing the interconnected oxygen atoms in the framework positions. They possess abundant of ordered channels and cages within molecular dimensional range, which can reversibly uptake the molecules (smaller than 1 nm) depending on the structure topology

[1–3]. Aluminosilicate zeolites display Brönsted acidity, due to the isomorphous substitution of tetrahedral Si atom by trivalent Al atoms in the framework positions, needing one proton ion to keep electron charge balance. As a result, Si–Al zeolites are widely used as acid catalysts, adsorbents, and ion-exchanges in petroleum refining and chemical manufacture [4–6]. Furthermore, to extend the application scope of zeolite, transition metal ions have been incorporated into the framework sites, with the endowment of redox property [7–9]. Up to now, the MFI-typed titanium silicalite-1 (TS-1) zeolite is the most successful and profoundly investigated one in the area of isomorphously substituted heteroatom zeolites. Since it is originally claimed by Enichem in 1983, TS-1 zeolite has attracted intensive attentions from both academic and industrial practices, owing to its high catalytic performance in hydrocarbon oxidation process. That is because the framework Ti species can enhance the nucleophilicity capability of H_2O_2 molecules to attack electrophilic groups during heterogeneous catalysis, through the acceptor–donator interaction between the empty $3d$ orbits of tetrahedral Ti species and electron pairs in H_2O_2 molecules [10–13]. Compared with traditional oxidation processes, TS-1 catalyzed routes are much more environmental friendly, with H_2O as the only side product. For example, the one-step cyclohexanone ammoximation approach by direct reacting with H_2O_2 and NH_3 has already replaced the conventionally four-step hydroxylamine routes in commercial ϵ -caprolactam production units [14–17].

However, at the early stage, TS-1 zeolite usually exhibited poor catalytic activity and reproducibility, due to the mismatch of hydrolysis and crystallization rates between Si and Ti species under hydrothermal conditions. To solve this problem, hollow titanium silicate (HTS) zeolite was developed by Lin and his coworkers at SINOPEC in 1990s, through a post-synthesis treatment in the presence of organic structure directing agents (OSDAs) [18–21]. It is found that HTS zeolite is of unique hollow cavities inside crystal, which are preferentially to enhance the mass diffusion property of reagents and products during catalytic reactions. Besides, the post-treatment promotes the hydrated condensation between Ti–OH and Si–OH groups, forming much more framework Ti species. Thus, HTS zeolite shows much higher catalytic performance than TS-1 zeolite in many oxidation reactions, such as phenol hydroxylation, cyclohexanone ammoximation, and propylene epoxidation and aromatic oxidation. On the other hand, HTS zeolite has its own intellectual property, which is very important to overcome patent restriction for its commercial production. Since 2000, SINOPEC has successfully completed the commercialization of HTS zeolite at a scale of 100 t/a. After that, HTS zeolite was initially used as catalyst for the environmental friendly cyclohexanone ammoximation process in the 140 kt/a commercial manufacture of ϵ -caprolactam at Baling Branch, SINOPEC, to replace the four-step HPO process, with low formation of toxic waste and side-products [22–25]. Thus, this route has been considered as one of the most important cases in green chemistry, due to its high atom utilization efficiency and low source consumption. Moreover, the HTS zeolite has also been employed in other industrial oxidation reactions, such as phenol hydroxylation and propylene epoxidation, with low concentration H_2O_2 solution as oxidant. Very recently, the 100 kt/a industrial demonstration plant of propylene epoxidation has been run smoothly, with high propylene oxide yield and H_2O_2 conversion.

Above all, HTS zeolite shows interesting physicochemical properties and great performance in the catalytic oxidation process, and we have done abundant of fundamental investigations to understand the basic principles in this topic, such as the hollow cavity characterization, chemical status of Ti species and the formation mechanism of constricted hierarchical structure. However, until now, the synthesis, characterization and catalytic application of HTS zeolite is still not reviewed systematically, especially for its catalytic performance in industry. Herein, we try to describe the main achievements on all aspects of HTS zeolite in brief, and we do hope it can provide a novel view for modifying zeolite materials to meet specific needs.

2. Synthesis and characterization of HTS zeolite

2.1. Synthesis of HTS zeolite through the “dissolution-recrystallization” treatment

TS-1 zeolite is the first crystalline transition metal inserted microporous materials (also referred to as heteroatom zeolites). As reported by Taramasso et al., TS-1 zeolite was synthesized using tetraethyl orthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH), and tetrabutyl orthotitanate (TBOT) as raw materials, under hydrothermal conditions and autogeneous pressure [18, 20]. The high pH value of TPAOH favors the existence of isolated Ti species coordinated by low aggregated Si species. The most important recipe for preparing particularly active TS-1 zeolite lies in the accurate control of the hydrolysis of Ti and Si sources in aqueous alkaline solution, to promote the formation of Si–O–Ti bonds, rather than Ti–O–Ti bonds. Although many alternative synthesis routes had been proposed by researchers over the past 30 years, except for Enichem Company, it is still difficult to prepare the active and stable TS-1 zeolite through direct method [26–29]. Consequently, to improve the catalytic performance of TS-1 zeolite, a novel post-synthesis treatment method has been designed by the researchers at SINOPEC in 1990s. In a typical procedure, the parent TS-1 zeolite is synthesized following the classic Enichem route as previously mentioned; and then the as-made TS-1 zeolite is calcined at high temperature in air to remove the organic templates inside micropores. In the next step, the calcined TS-1 zeolite is washed by specific additive agents, for trying to remove the extraframework Ti species (majorly in the form of anatase TiO_2); after that, this TS-1 zeolite is mixed with aqueous TPAOH solution, and sealed in a Teflon autoclave. Then, the autoclave is continuously heated at high temperature (usually over 120°C) under statistic state for several days, with the formation of white HTS zeolite powder. It is worthy noted that the as-made TS-1 zeolite, which containing TPAOH template, cannot be used as precursor to prepare HTS zeolite treated under the same procedure as calcined TS-1 zeolite. Thus, it is inferred that part of TS-1 zeolite is dissolved in the alkaline solution, and the soluble Si and Ti species are recrystallized under the impact of TPAOH molecules during the post-synthesis processing. Most importantly, this post-synthesis treatment is very convenient and available in both laboratory and industry, on which allows the commercial manufacture of HTS zeolite at large scale.

2.2. Confirmation of hollow cavities and reincorporation of Ti species

It is well known that the intracrystalline porosity is of great importance to enhance the catalytic performance of zeolites during heterogeneous reactions [30–32]. Different from TS-1 zeolite, HTS zeolite shows a typical H_2 hysteresis loop at the region of P/P_0 between 0.45 and 1 in the N_2 physisorption curve (**Figure 1**), which suggests the existence of ink-bottle like hierarchical pores. It is attributed to the tensile strength effect, owing to the difference between capillary condensation for adsorption and capillary evaporation for desorption. The hysteresis loop starting from $P/P_0 = 0.45$ usually reveals the constricted mesopores and/or macropores inside zeolite crystal [33–35]. Thus, to further confirm the feature of hierarchical pores, transmission electron microscopy (TEM) method has been used, as illustrated in **Figure 2**. Obviously, abundant of hollow cavities (around several to tens nm in size) have been observed in the HTS zeolite, while the conventional TS-1 zeolite is completely solid. Moreover, to learn the three dimensional distribution of hollow cavities, HTS zeolite was characterized by using electron tomography (ET) technology [36–38]. As displayed in **Figure 2b** (insert), intracrystalline cavities are highly dispersed inside HTS zeolite with different size and shape. Consequently, we can infer that intracrystalline pores have been created via the post-synthesis treatment in the presence of template under hydrothermal conditions. Herein, it is noted that HTS zeolite is still of high crystallinity and uniform morphology, which are favor of the high stability during catalytic process. Therefore, this post-synthesis route takes much more advantages than base/acid leaching method and provides a novel strategy to design and modify zeolite materials for meeting specific demands in heterogeneous catalysis.

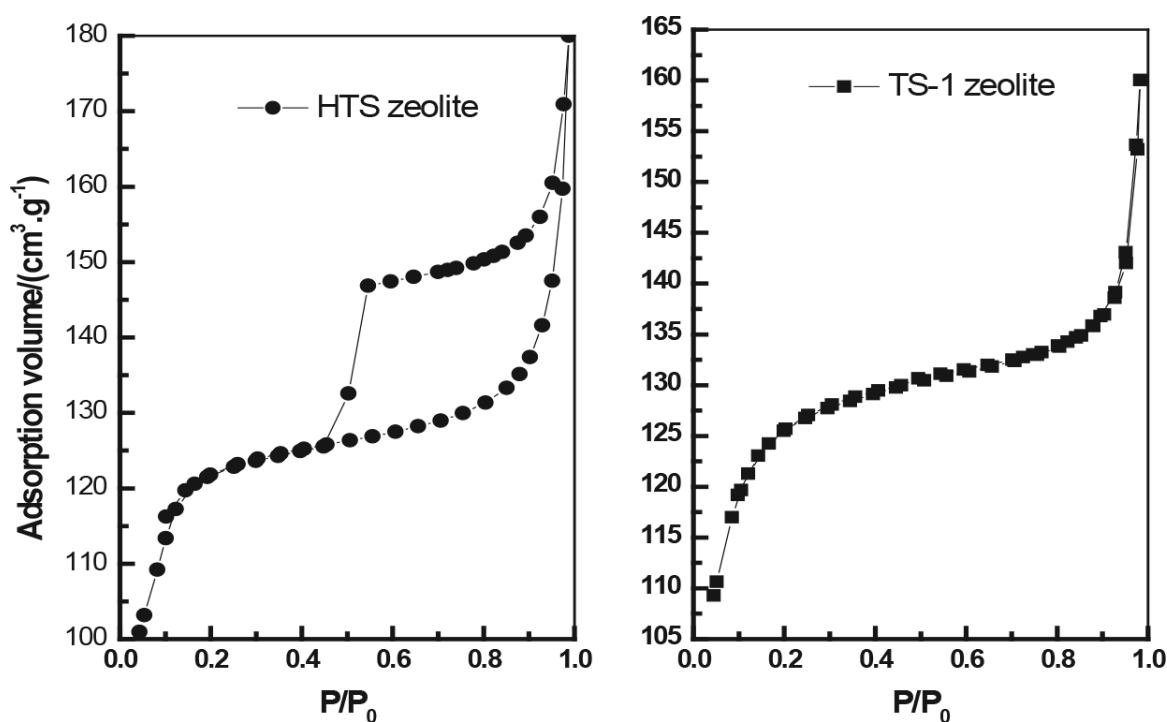


Figure 1. Low-temperature N_2 adsorption-desorption curves of HTS and TS-1 zeolites.

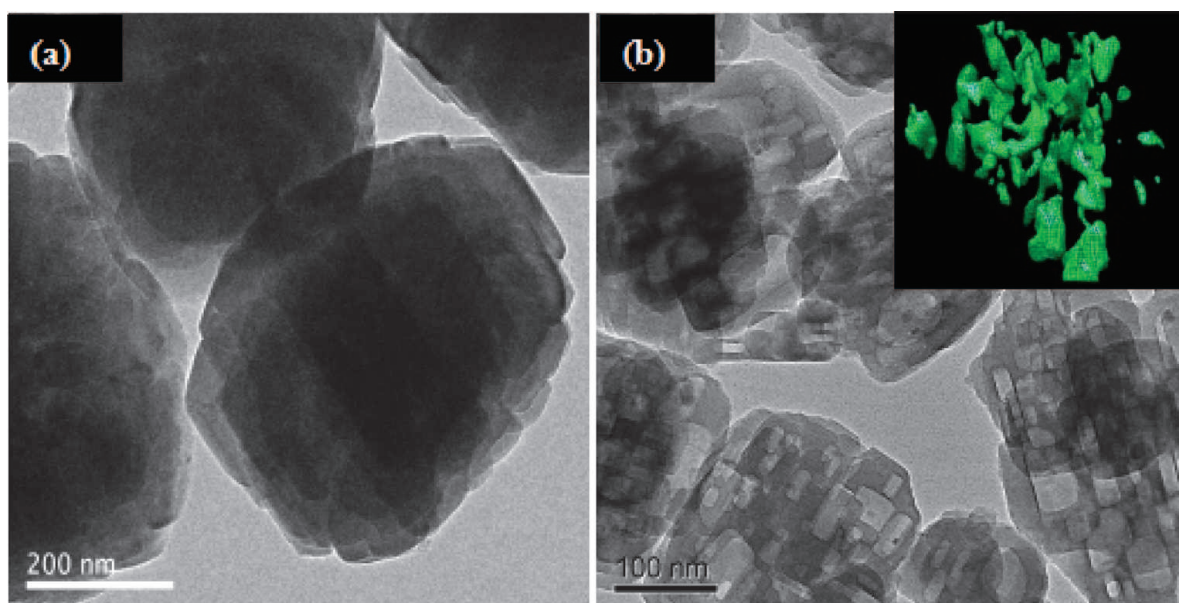


Figure 2. (a) TEM image of conventional TS-1 zeolite, (b) TEM image of HTS zeolite, and the restructured image of hollow cavities (insert).

Besides the formation of hollow cavities, the reincorporation of Ti species into framework positions has also been found in our previous work. Firstly, the chemical status of Ti species in the HTS zeolite has been distinguished by X-ray photoelectron spectroscopy (XPS) through peak fitting treatment [39, 40]. Apparently, two kinds of Ti species, referred to as framework Ti and extraframework Ti species, have been detected in the external surface of HTS zeolite (as presented in **Figure 3**). That is because the chemical environment of Ti atoms in the framework positions are different from that in the extraframework Ti species, especially for octahedral anatase TiO_2 crystal.

Additionally, it is widely accepted that the band at around 960 cm^{-1} in the FT-IR spectrum is attributed to the stretching vibration of Si–O–Ti bonds, indicating the incorporation of tetrahedral framework Ti species. And the band intensity ratio between 960 and 800 cm^{-1} (I_{960}/I_{800}) is relevant with the framework Ti content [41, 42]. Thus, it is concluded more tetrahedral Ti species have been inserted into framework sites after the post-synthesis treatment, due to the higher I_{960}/I_{800} value of HTS than that of TS-1 zeolite (as shown in **Figure 4**). Furthermore, to verify the reincorporation of Ti species, ^{29}Si MAS NMR spectroscopy has been employed to detect the chemical environment of Si species, which can indirectly give the information on the chemical status of Ti species. Generally, the bands at around -113 and -116 ppm are ascribed to the framework $\text{Si}(\text{OSi})_4$ and $\text{Si}(\text{OTi})(\text{OSi})_3$ species, respectively, owing to induction effect of framework Ti atoms substituted Si atoms [43–45]. As shown in **Figure 5**, HTS zeolite has a larger peak at -116 ppm than TS-1 zeolite, and thus it is well demonstrated that “dissolution-recrystallization” treatment favors the reincorporation of tetrahedral Ti species into framework sites.

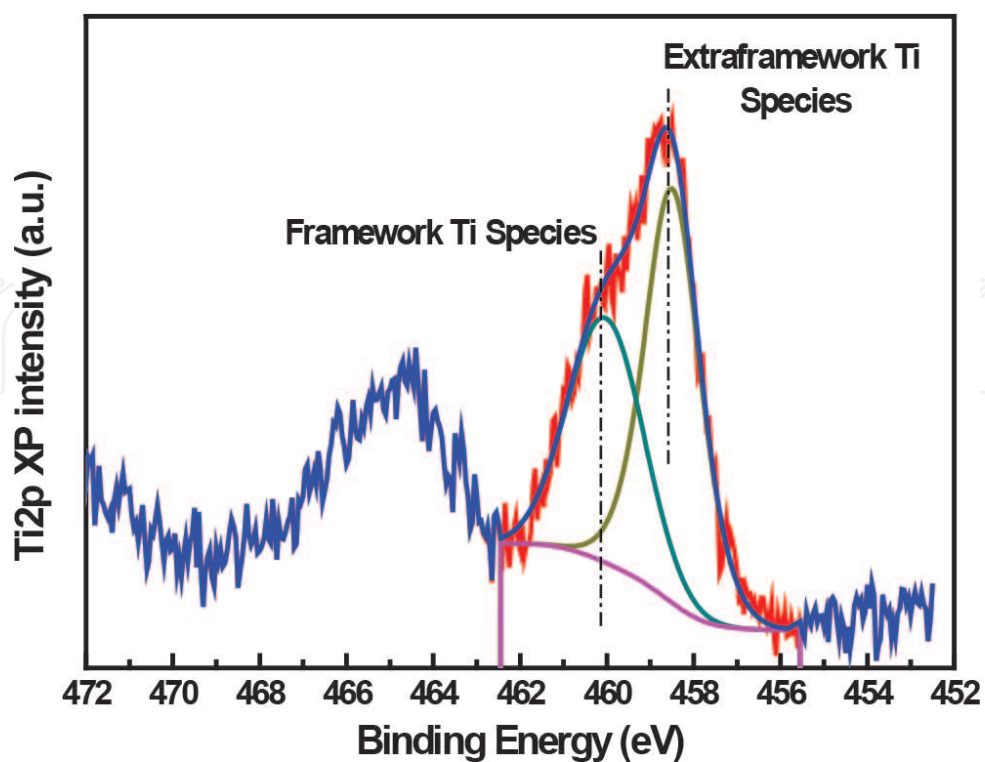


Figure 3. XPS spectrum of HTS zeolite with peak fitting to confirm framework and extraframework Ti species.

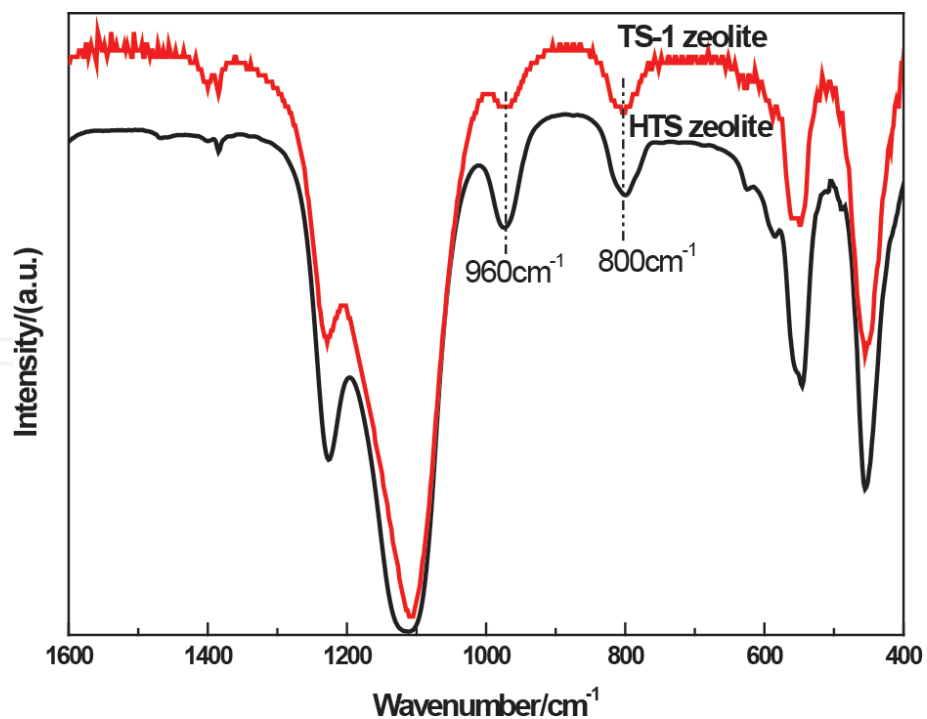


Figure 4. FT-IR spectra of both TS-1 and HTS zeolites.

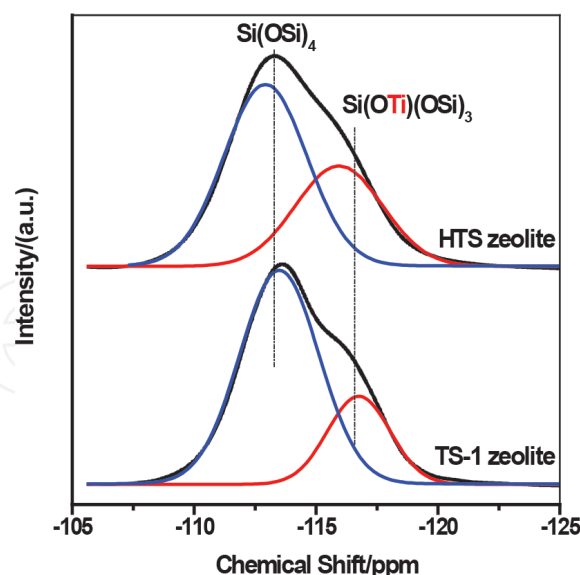


Figure 5. ^{29}Si MAS NMR spectra of both TS-1 and HTS zeolites.

2.3. The formation mechanism of hollow voids inside HTS zeolite

The detailed formation mechanism of hollow cavities inside zeolite is still not fully understood, but huge investigations on this post-synthesis treatment have been carried out. To certify the “dissolution-recrystallization” process, the as-made (organic template containing) TS-1 zeolite was treated by using three different methods, as following: (a) the as-made TS-1 zeolite was post-synthesized in the TPAOH solution at high temperature; (b) the as-made TS-1 zeolite was calcined to remove organic template, and then treated in the TPAOH solution at 80°C in air;

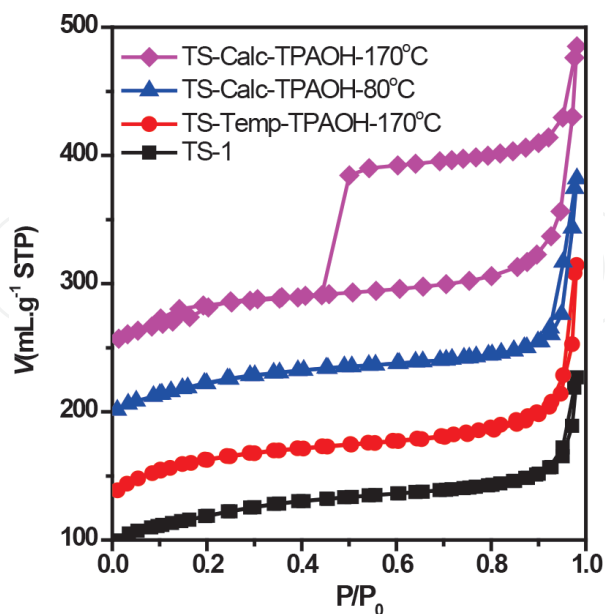


Figure 6. Low-temperature N_2 adsorption-desorption curves of different titanium containing zeolites.

(c) the as-made TS-1 zeolite was calcined to remove organic template, and then post-synthesized in the TPAOH solution at 170°C under autogeneous pressure. **Figures 6 and 7** show the N₂ physisorption curve and TEM characterization results of these mentioned samples. We can observe that only the calcined TS-1 zeolite can be used as starting material to prepare HTS zeolite under hydrothermal conditions.

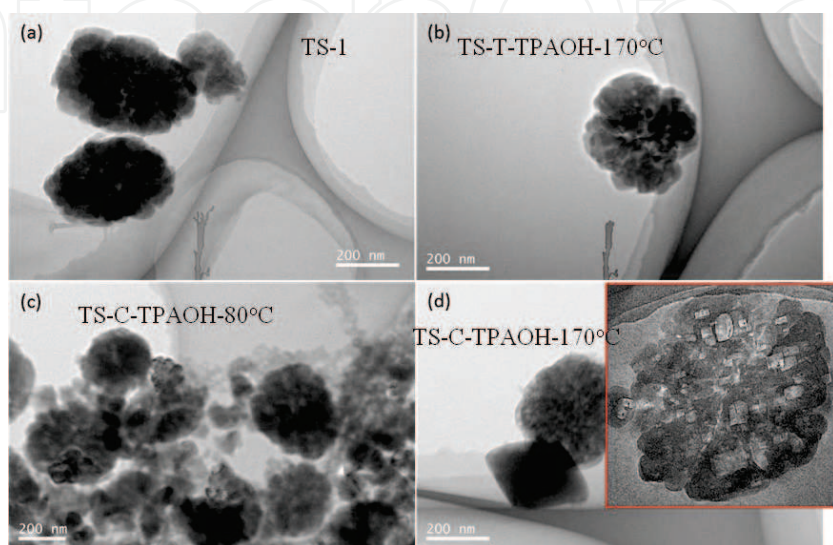


Figure 7. TEM images of different titanium containing zeolites.

On the formation mechanism of hollow cavities, Mielby et al. has ever used cetyltrimethylammonium bromide (CTAB) alkaline solution as organic structure directing agent (OSDA) to produce the Silicalite-1 zeolite with hollow voids [46–48]. They consider that the CTAB molecules can enter into the bulk body of zeolite to form micelles, which serves as the mesoporous template for hollow structure via directing the soluble Si and Ti species dissolved from zeolite crystal. However, this viewpoint is not fully reasonable enough to demonstrate the generation of hollow cavities inside HTS zeolite, owing to the larger molecular diameter of TPAOH than that of CTAB molecules. On the other hand, CTAB is of poor capability to cause the formation of MFI topology. Based on these mechanistic models, one plausible mechanism has been proposed to explain the formation of hollow cavities inside zeolite during “dissolution–recrystallization” process, but it still needs further detailed analysis results to support it. We consider that, in the initial stage, the calcined TS-1 zeolite can be dissolved in the TPAOH solution to, owing to the hydrolysis of T–O–T bonds (T stands for the framework atoms) catalyzed by OH[−] anions in both external surface and bulk body of zeolite. It is worthy to note that only OH[−] anions, rather than TPA⁺ ions, go into zeolite body along microporous channels. Due to the absence of TPA⁺ ions, the recrystallization of soluble Ti and Si sources cannot be occurred, without the formation of new TS-1 inside zeolite crystal. At the same time, the “dissolution–recrystallization” process happens in the external surface, with the changing of zeolite morphology. That is why the hollow voids cannot be produced for the post-synthesis of template-containing TS-1 zeolite, which is ascribed to the restriction

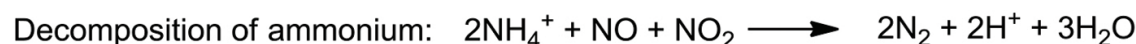
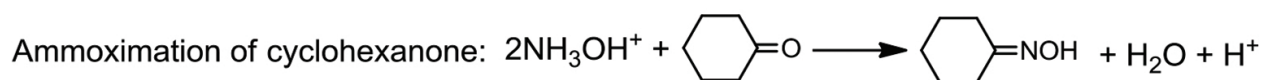
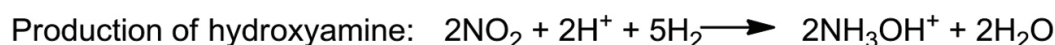
of mass transfer of OH⁻ group within zeolite. Above all, this proposed mechanism provides a novel view for describing the formation hollow structure, which is in favor of the inner diffusion of raw materials and products during catalytic oxidation processing [49–51].

3. Applications of HTS zeolite in catalytic oxidation processes

3.1. Cyclohexanone ammoximation process

Cyclohexanone oxime, produced by cyclohexanone ammoximation, is one of the most important chemical intermediates to produce ε-caprolactam via a Beckmann intramolecular rearrangement [52–54]. ε-caprolactam is widely used to manufacture nylon-6 worldwide, which acts as the precursor for producing fiber, plastic, resins, so on. As the fast development of human society, especially for recent 10 years, the demands of ε-caprolactam and cyclohexanone oxime are becoming rapidly increasing. The traditional cyclohexanone oxime production methods majorly focus on the hydroxylamine phosphate (HPO) or hydroxylamine sulfate (HSO) routes, as shown in **Figure 8a** [55–57]. Obviously, it is very complex, highly polluted and corrosive to prepare hydroxylamine, which is used as oxidant for cyclohexanone ammoximation reaction, due to the usage of strong acid solutions and ammonia. Large amount of low value-added side-products (particularly ammonium sulfate) are formed in this approach, and thus the traditional methods obey the fundamental principles of green chemistry and need to be remarkably improved in both academia and industry.

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



(b) *"One-step" method*

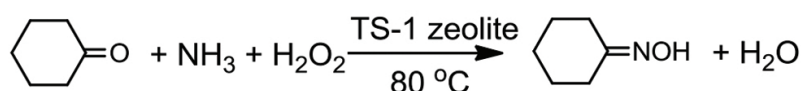


Figure 8. Reaction pathways of traditional HPO route (a) and one-step route catalyzed by TS-1 (b).

To overcome these drawbacks in HPO and HSO routes, a new liquid phase one-step process was developed by Enichem in 1987 [58–60]. It is based on the “one-step” cyclohexanone ammoximation of catalyzed by TS-1 zeolite, with ammonia and hydrogen peroxide solutions

as reactants, as demonstrated in **Figure 8b**. After that, extensive researches have been carried out with make this novel route become economic and technological available in industry. Compared with traditional routes, there is no hazard side-product generated in the TS-1 catalyzed route, with water as the only by product and the atom efficiency over 85%. Here, the cyclohexanone oxime can be achieved by one-step method, which is operated under mild condition, with low reaction temperature and low pressure. Therefore, cyclohexanone ammoximation reaction catalyzed by TS-1 zeolite is considered as a completely environmental-friendly process.

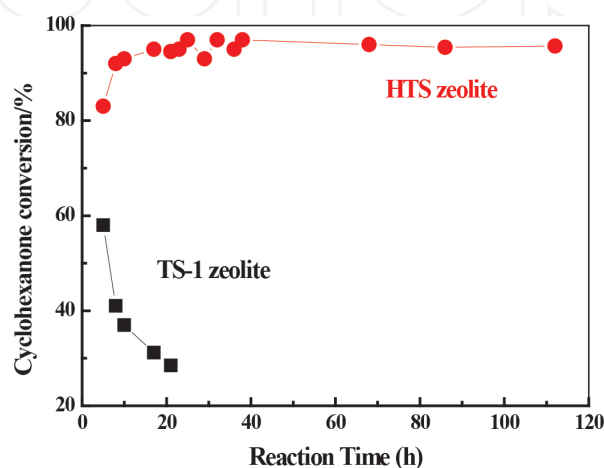


Figure 9. Catalytic performance of TS-1 and HTS zeolites in the cyclohexanone ammoximation with low concentration H_2O_2 solution as oxidant.

However, the TS-1 zeolite synthesized by traditional method is usually of poor catalytic performance in cyclohexanone ammoximation process, due to the presence of alkaline ammonia, causing the hydrolysis of Ti–O–Si bonds. Thus, in the early years, the stability of TS-1 zeolite was considered as the main obstacle to prevent this process be commercialized at large scale, which was attributed to the low lifetime of TS-1 zeolite in ammoximation system. That is why only first one 12 kt/a cyclohexanone ammoximation demonstration installation was established by Enichem in 1994 at Porto Margherita, Italy [61]. With respect to the deactivation of TS-1 zeolite, three main aspects were proposed by Petrini et al., such as (a) pore filling by heavy organic side-products, (b) the transformation of framework Ti atoms into extraframework Ti species, and (c) dissolution of framework Si atoms in the alkaline solution [62–65]. And very recently, we have confirmed this phenomenon using multiple characterization methods and catalytic evaluation. Therefore, to enhance the stability of TS-1 zeolite in ammoximation, the HTS zeolite was developed by Lin et al., at SINOPEC through a novel post-synthesis of conventional TS-1 zeolite in the presence of TPAOH under hydrothermal condition. The catalytic performance of HTS and TS-1 zeolites in cyclohexanone ammoximation process is outlined in **Figure 9**, which suggests that HTS zeolite displays much higher catalytic activity and longer lifetime than conventional TS-1 zeolite under the same reaction conditions. In our opinion, the fast cyclohexanone conversion rate is attributed to the generation of hollow voids inside crystal, which favors the accessibility of raw material molecules to tetrahedral

framework Ti sites, and improves inner mass diffusion, thus reducing the formation of heavy organic deposit. And the high stability of HTS zeolite is associated with the reincorporation of Ti species into the framework positions via the dehydrated condensation between Ti-OH and Si-OH groups under hydrothermal conditions. As shown in **Figure 9**, the lifetime of HTS zeolite in ammoxidation reaction is much longer than that of TS-1 zeolite, with high cyclohexanone conversion (>95%) for over 110 h. As a result, the commercial cyclohexanone ammoxidation units catalyzed by HTS zeolite had been builded in Baling Petrochemical Company, SINOPEC at 140 kt/a scale since 2000, to replace the conventional four-step HPO process. In industrial process, the cyclohexanone conversion and oxime selectivity are all higher than 99.5%, whereas the utilization efficiency of H_2O_2 is about 90%. It is worthy to note that the size of HTS zeolite is about 200–350 nm, which means these particles are hard to be separated from reaction system. Thus, the separation process of HTS zeolite by inorganic member was been successfully developed and widely applied in industrial ammoxidation units. In a word, this novel route takes promising advantages for the manufacture of ϵ -caprolactam, with significant economic and environmental meaning. Additionally, in very recent years, several cyclohexanone ammoxidation units catalyzed by HTS zeolite have been established or are still under construction, with even larger scale (>200 kt/a) in China.

3.2. Phenol hydroxylation process

Phenol hydroxylation to prepare catechol (*o*-dihydroxybenzene) and hydroquinone (*p*-dihydroxybenzene), which are widely applied to manufacture agrichemical, photography chemicals, antioxidants, polymerization inhibitors, is one of most important reactions in fine chemical industry [66, 67]. Traditionally, catechol, usually together with hydroquinone, is produced by oxidation of phenol with various oxidants, such as 60–70% aqueous H_2O_2 solutions, performic acid, and ketone peroxides (such as α -hydro hydroperoxides). Heavy transition metal compounds and strong phosphoric acid are selected as catalysts for these hydroxylation reactions, but they are very difficult to be separated from products [68, 69]. Obviously, these processes are very complicated and far beyond environmental friendly to be carried out at commercial scale, with very low atom utilization efficiency. There are huge amount of liquid and/or solid phase wastes need to be disposed, which are highly toxic and corrosive for the installations. Fortunately, one completely green and clean phenol hydroxylation process via using TS-1 zeolite as catalyst has been developed by EniChem, which uses low concentration (usually 30 wt%) H_2O_2 solution, and is carried out under benign conditions (lower than 100°C and atmosphere pressure). **Figure 10** shows the comparison of catalytic performance of HTS and TS-1 zeolite in phenol hydroxylation under the same conditions. We observe that HTS zeolite can faster catalyze the transformation of phenol than TS-1 zeolite, which is correlated with its inner hierarchical structure. That is to say, hollow cavities promote the mass diffusion inside zeolite crystal, while the higher phenol conversion is dependent on the more framework Ti content, as previously characterized. Based on the excellent catalytic performance, several phenol hydroxylation installations have been builded and run smoothly in China.

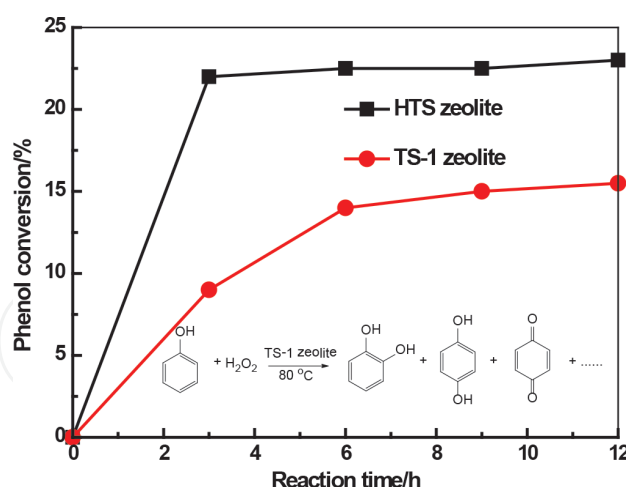


Figure 10. Catalytic performance of HTS and TS-1 zeolite in phenol hydroxylation reaction.

Furthermore, the phenol hydroxylation is chosen as probe reaction to reveal the kinetic activity of framework Ti sites, owing to its mechanism on the activation of H_2O_2 , rather than functional groups in phenol. Although high-concentration (>60 wt%) H_2O_2 solutions are of strong nucleophilic attack capability during catalytic oxidation reaction, it is considerably difficult and dangerous to store, transfer and use them at large scale. Interestingly, the activated H_2O_2 molecules (in the form of Ti-OOH species) by HTS zeolite are of as strong nucleophilicity as 60 wt% H_2O_2 solution or peroxide acids. And the solid HTS zeolite crystal is easy to be separated from liquid phase, and thus the heterogeneous hydroxylation process has attracted kind attentions from the researchers in both academic and industrial sections.

3.3. Propylene epoxidation (HPPO) process

Propylene oxide (PO) is also one of the most important chemical intermediates to produce polyesters and polyurethane in industry, with an increasingly huge market worldwide (over 7.5 million tons in 2010) [70–73]. Generally, two basic strategies are majorly employed for commercial PO production, including hydrochlorination route and co-oxidation route. The former one involves the transformation of propylene to chloropropanols and dehydrochlorination, which need to use the Cl_2 and $\text{Ca}(\text{OH})_2$ as basic materials, respectively, with the formation of corrosive and low value-added wastes. The other one lies in the co-oxidation of propylene and other organic compounds (such as ethylbenzene or isobutane) with air or O_2 as oxidant, in the presence of catalyst. The coproducts in this route are t-butyl alcohol, MTBE or styrene, but the main drawback is the high capital and material cost and long reaction pathway. To avoid these disadvantages, an ultra environmental-friendly propylene epoxidation process with hydrogen peroxide as oxidant (referred to as HPPO route) was exploited by using TS-1 zeolite as catalyst, and in 2009 a new HPPO plant was started up by BASF and Dow chemical at 300 kt/a scale in Antwerp [74–77]. Later on, several HPPO plants were established in many countries, such as Korea, Thailand, and China. At the same time, the HPPO process catalyzed by HTS zeolite has been developed by SINOPEC, and one 100 kt/a propylene epoxidation industrial initialization has been established and run smoothly in China.

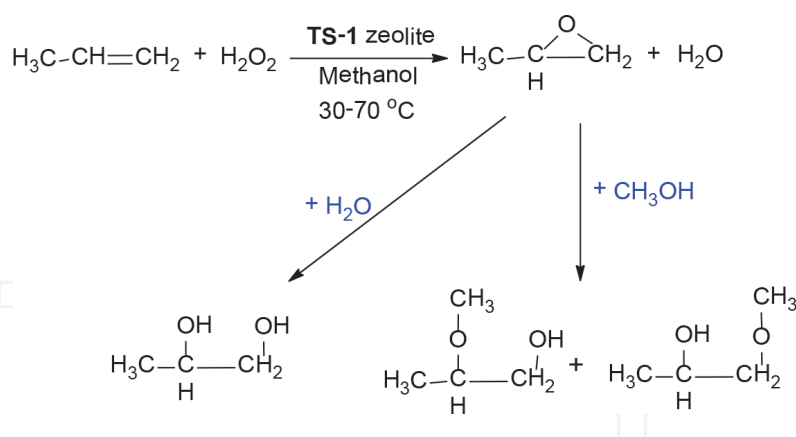


Figure 11. Reaction network of propylene epoxidation via HPPO process.

With respect to the reaction network of HPPO process, except for the major propylene epoxidation, other side reactions (as shown in **Figure 11**) are also happened, causing the decrease of PO yield. Thus, it is necessary to use large amount of methanol as solvent and operate this route at low temperature. A 1.0 kt/a HPPO process, schematic flow diagram is demonstrated in **Figure 12**. The epoxidation reaction is carried out in a fixed-bed reactor, with the mixture of propylene and H_2O_2 injecting into the reactor. When the epoxidation reaction at 1.0 kt/a scale is carried out in a wide range, $T = 30\text{--}70^\circ\text{C}$, $P = 0.5\text{--}2.0 \text{ MPa}$, WHSV of H_2O_2 molecules is $0.12\text{--}1.2 \text{ h}^{-1}$, $n(\text{CH}_3\text{OH})/n(\text{H}_2\text{O}_2)$ is $5\text{--}25$, $n(\text{Propylene})/n(\text{H}_2\text{O}_2)$ is $1.2\text{--}2.5$, the TOF of H_2O_2 is around $31\text{--}32 \text{ mmol g}^{-1} \text{ h}^{-1}$ ($X_{\text{H}_2\text{O}_2}$ is $96\text{--}99\%$) and selectivity of PO is $96\text{--}99\%$, which is much better than that reported by BASF and DOW (the selectivity of PO is 93.2%). Furthermore, the raw propylene oxide produced in the fixed-bed reactor is purified in the PO purification column, obtaining the final PO product at 99.97% purity. And then, the purified PO has been used as chemical intermediates to manufacture 1,2-ethyl glycerol, oilfield demulsifier, propylene carbonate, triisopropanolamine, hydroxypropy, and dimethyl carbonate [78].

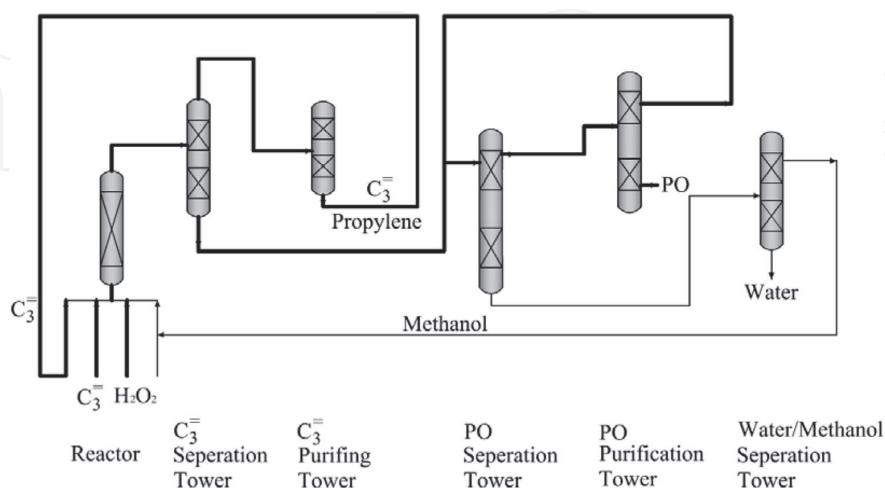


Figure 12. Schematic process flow diagram of propylene epoxidation at 1.0 kt/a pilot scale [78].

3.4. Baeyer–Villiger oxidation of cyclohexanone

Baeyer–Villiger (B–V) oxidation is an important reaction to produce esters or lactones from ketones via inserting one O atom in C–C bond. Especially, ϵ -caprolactone, prepared via cyclohexanone BV oxidation, is widely used to synthesize polycaprolactone and poliglecaprone [79–83]. Traditionally, many kinds of peracids, such as *m*-chloroperbenzoic acid, trifluoroperacetic acid and perbenzoic acid, are chosen as oxidizing agents and catalyst to motivate BV reaction. The main advantages are the high ketone conversion and fast transformation rate, but there are still many significant drawbacks, such as low selectivity of target products, low atomic utilization, being harmful to the environment and dangerous to handle. Thus, up to now, only three companies can commercially produce ϵ -caprolactone based on peracids oxidant in the world, owing its long and complex reaction pathway. To beat these drawbacks, low concentration (usually 30–50 wt%) H_2O_2 solution (which cheap and easy to handle) is considered as the best candidate to hazardous replace peracids. But it is of poor nucleophilic capability to attack the carbonyl group in ketones during BV oxidation reaction. As a result, two basic strategies are proposed to accelerate the heterogeneous B–V oxidation of cyclohexanone using aqueous H_2O_2 solution: (a) activation the carbonyl groups to make the C atoms in carbonyl group easy to be attacked by H_2O_2 molecules; (b) increasing the nucleophilic capability of H_2O_2 molecules by forming M-OOH species (M represents transition metal element, which could accept the lone electron pairs by employing their empty *d* orbitals) [84, 85].

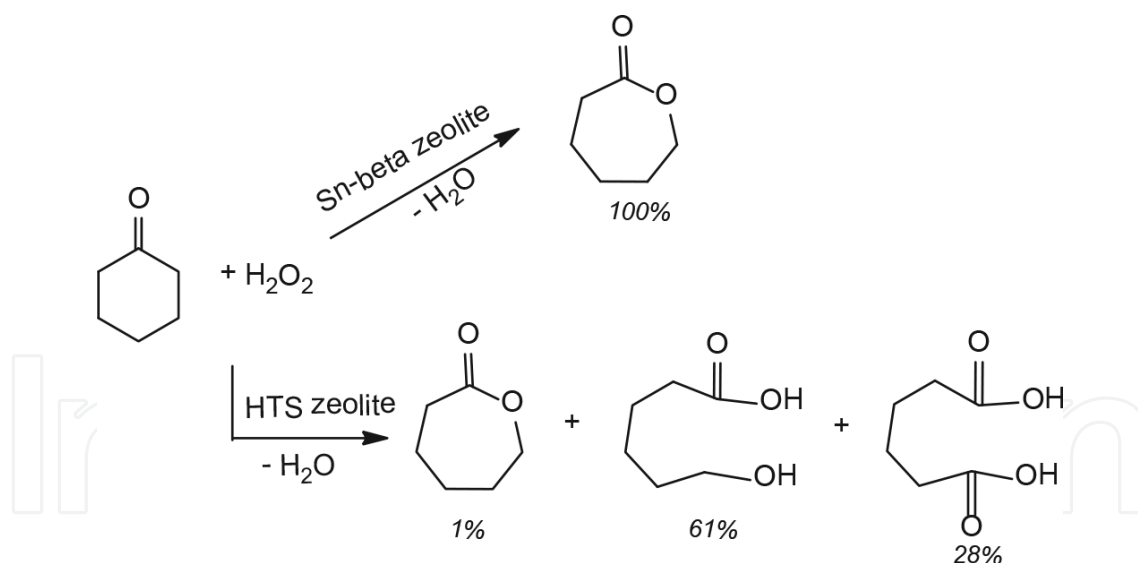


Figure 13. BV oxidation of ketones with different zeolite catalysts under mild reaction conditions [86, 87].

For activation of carbonyl group, Sn-beta zeolite reported by Corma and his coworkers [88–90] shows the most promising catalytic performance in BV oxidation of cyclohexanone with low concentration H_2O_2 solution, with almost 100% ϵ -caprolactone selectivity. It is attributed to the tetrahedral coordinated Sn atoms that were incorporated into the framework of beta zeolite can accept the electron pairs in carbonyl group of cyclohexanone. On the other hand, TS-1 zeolite is extensively confirmed as the Lewis catalyst to activate H_2O_2 molecules.

Consequently, HTS zeolite is taken as catalyst to promote the BV oxidation of cyclohexanone under mild conditions, as show in **Figure 13**. It suggests that HTS zeolite has the different product distribution from the Sn-beta zeolite, with high selectivity of deep-oxidative products, which are 6-hydroxyhexanoic acid and adipic acid. 6-hydroxyhexanoic acid is produced through the ring-opening reaction of lactone, due to the poor stability of 7-member ring of ϵ -carprolactone and high water content in reactor. Then, the C-OH groups in 6-hydroxyhexanoic acid can be further oxidized by Ti-OOH species, to obtain the C-OOH group in adipic acid [86]. Compared with Sn-beta catalyzed route, HTS-catalyzed reaction system does not use any specific organic solvents, which lower the concentration of oxidant and are high-energy consumed to be separated. Thus, it is in favor of the formation of a series of important chemical intermediates in this “one-pot” reaction. However, there are still many kinds of undesirable by-products formed at the same time, reducing the yields of target product. As a consequence, the BV oxidation of cyclohexanone catalyzed by HTS zeolite is still under investigation in the laboratory to minimize other side reactions.

3.5. Catalytically selective oxidation of cyclohexane

Cyclohexane oxidation is an ultra important reaction to product KA oil (including cyclohexanone and cyclohexanol) in industry, for manufacturing various of chemical precursors and final products, as shown in **Figure 14**. Generally, the KA oil is usually obtained via these methods: hydrogenation of phenol, hydration of cyclohexene, hydrogenation of benzene, and air oxidation of cyclohexane (>90% for KA oil production) [91–94]. The cyclohexane oxidation with air or O_2 can be carried out in the presence of various catalysts or in the absence of catalyst, with high temperature (>100°C) and autogeneous pressure. Although air is very cheap and easy to be obtained, this route also suffers serious restrictions in industrial practice, such as low yield of target product, high pollution and waste generation, and particularly high-energy consumption needed for separation of products.

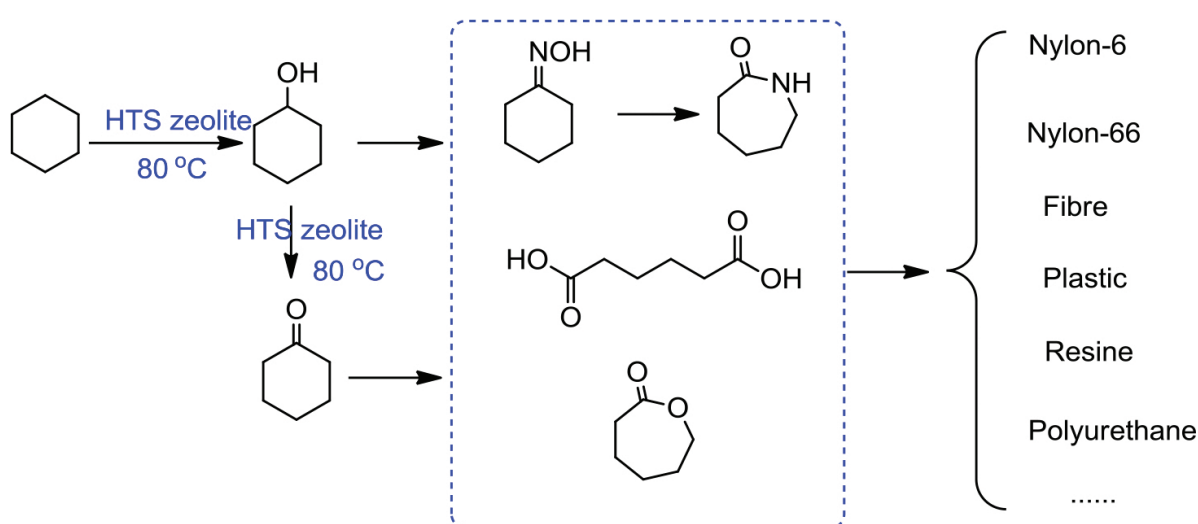


Figure 14. Reaction pathway of oxidation of cyclohexane catalyzed by HTS zeolite with H_2O_2 solution.

For solving these limitations, cyclohexane oxidation with H_2O_2 catalyzed by TS-1 zeolite has also been investigated. It is found that the KA oil can be achieved through this approach, with very high cyclohexane conversion and selectivity of KA oil under mild conditions. Herein, HTS zeolite is also introduced to catalyze the cyclohexane oxidation, as illustrated in **Figure 15**. We observe that the total yield of KA oil is increasing as a function of reaction time, which is up to 70% after reaction time more than 10 h. The optimized reaction parameters are as follow: $T = 60\text{--}80^\circ\text{C}$, catalyst content = 5–10%, cyclohexane to H_2O_2 molar ratio = 0.5, acetone to cyclohexane molar ratio = 10–15, reaction time = 6–10 h. Under this conditions, the yield of KA oil is over 40%, with a cyclohexanone/cyclohexanol ratio larger than 2. Above all, the cyclohexane oxidation catalyzed by HTS zeolite shows great industrial potential, and the further study on scale up of this route is still under carrying out [95, 96].

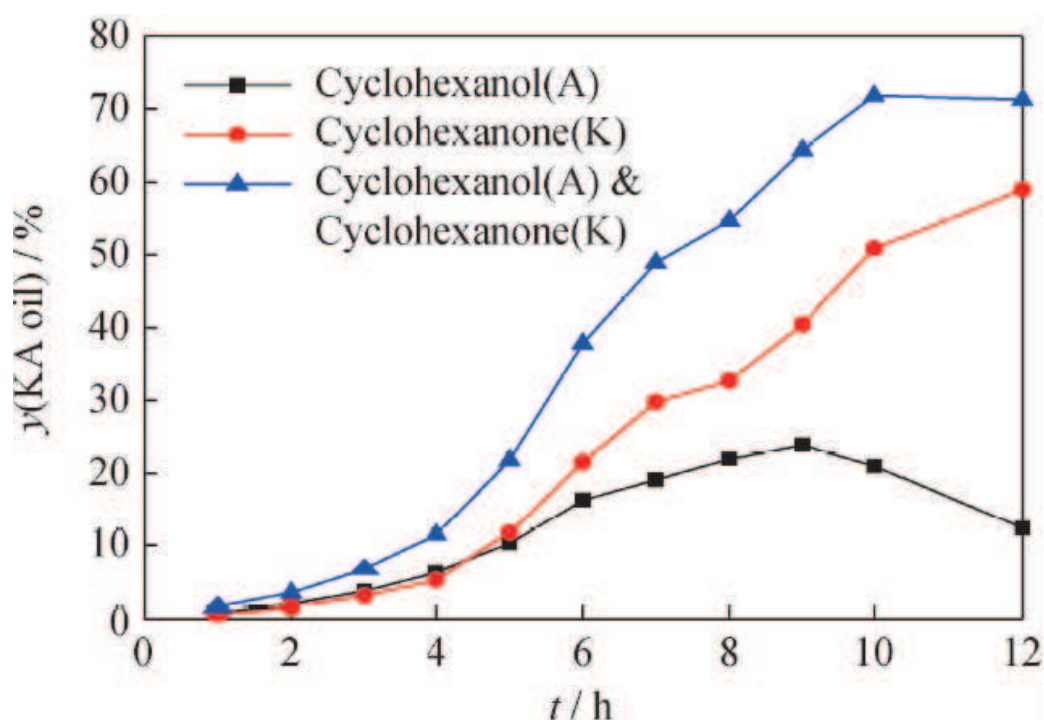


Figure 15. Catalytic performance of HTS zeolite in cyclohexane oxidation with H_2O_2 solution [95].

3.6. Catalytic oxidation of aromatic compounds

Aromatic oxidation is of great important, but still a big challenge in the chemical industry, because the kinds and quantity of synthetic aromatic compounds demanded are so huge in the world. Several synthesis methods have been developed for the oxyfunctionalization of aromatics, such as the partial oxidation of isopropylbenzene, neutralization of benzenesulfonate, hydrolysis of chlorobenzene, direct oxidation with N_2O , and direct oxidation with H_2O_2 solution [97–100]. among them, the last two routes are considered as typical green chemistry process, but the origination of N_2O is so limited.

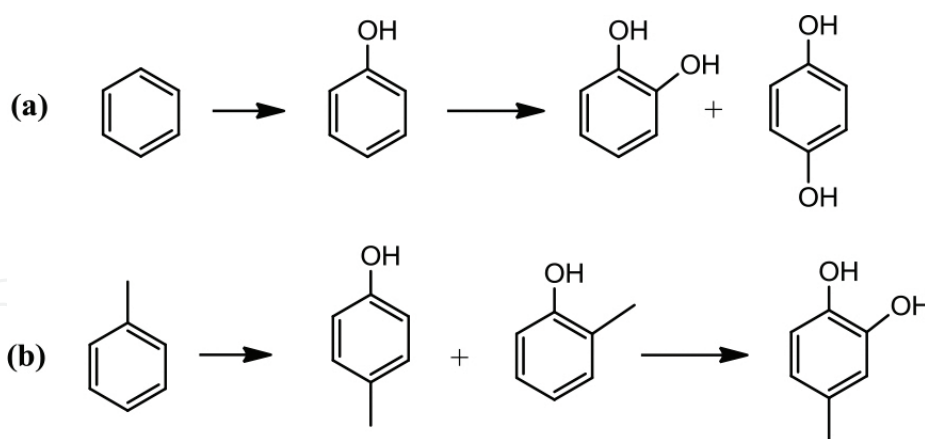


Figure 16. Reaction pathway of aromatic oxidation with H_2O_2 solution catalyzed by HTS zeolite.

In our laboratory, both benzene and toluene oxidation reactions catalyzed by HTS zeolite have been examined (**Figure 16**), which show some aromatic conversion and high selectivity of target product [101, 102]. And it is found that polar solvents are useful for high conversion rate, but the high intersolubility between aromatics and H_2O_2 is still very difficult. Thus, it is necessary to intensify the mixing inside various reactor.

4. Conclusion and perspective

In summary, HTS zeolite, which synthesized via “dissolution–recrystallization” treatment, is an innovative catalytic material for the conversion of oxygenated hydrocarbons under mild conditions. It has been well demonstrated that highly dispersed intracrystalline mesopores and/or macropores are formed inside zeolite, which favors the inner mass diffusion and high conversion rate confirmed by physicochemical adsorption of N_2 and catalytic evaluation. The mechanism of the formation of these hollow cavities has been proposed to further understand the “dissolution–recrystallization” process, which involves the diffusion of OH^- group inside zeolite crystal to form hollow voids, and the recrystallization of soluble Ti and Si sources cause the change of zeolite morphology. At the same time, the reincorporation of Ti species into framework positions has been verified using multiple characterization methods, with the significantly decreasing of framework defects (Q^3 Si species) and increasing of framework Ti content. That is why HTS zeolite shows even longer lifetime than conventional TS-1 zeolite in alkaline cyclohexanone ammoximation reaction, owing to relative perfect framework atoms tolerated to basic corrosion, except for the fast mass transfer via hierarchical structure. Since 2000, HTS zeolite has been successfully commercialized by SINOPEC in China.

Based on the unique hollow feature and high framework content, HTS zeolite displays very excellent catalytic performance and stability in many selective oxidation reactions of organic compounds, that is, cyclohexanone ammoximation, phenol hydroxylation, propylene epoxidation, Baeyer–Villiger oxidation of cyclohexanone, selective oxidation of cyclohexane

and benzene, so on. The first three items have been already put into commercialization to produce bulk chemicals by SINOPEC, of great social and environmental significance to reduce pollution in industry. The others are still under investigation in the laboratory, but some ones have present good potential to replace these hazard and low atom efficiency process. For further development of HTS zeolite material and its catalytic application, we consider that the synthesis and modification of HTS zeolite should be paid more attention, because catalytic materials are the fundamentally original power for the development of heterogeneous catalysis. Moreover, the fast development of chemistry science and human society provides so many opportunities for catalytic materials with specific characteristics. Thus, from the viewpoint of application, HTS zeolite still has considerable applications in the conversion of oxygenated hydrocarbons, such as in fine chemical, environmental catalysis, and biomass utilization. Additionally, combining the redox property of HTS with other functions (such as hydrogenation of noble metal, Pt or Pd) is also a good way for updating its application. In a word, this chapter is of both theoretical and practical meanings to design and produce catalytic materials for facing specific demands. We have described a systematical investigation on zeolite synthesis and environmental-friendly heterogeneous catalysis processes from laboratory to large commercial scale.

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