# Catalytic monoepoxidation of butadiene over titanium silicate molecular sieves TS-1

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Titanium silicate molecular sieves TS-1 have been prepared under hydrothermal conditions with tetrapropylammonium hydroxide as structure-directing agent. The structures of TS-1 were characterized by means of XRD, TEM, FT-IR, DR UV-Vis, ICP-AES, and $N_2$ adsorption/desorption techniques. Its catalytic performances in the epoxidation of butadiene with hydrogen peroxide were investigated; 3,4-epoxy-1-butene was obtained with high selectivity. The influences of various parameters such as temperature, solvent, and titanium content on the activities of the catalysts were studied systematically.

**Keywords:** 1,3-butadiene, epoxidation, 3,4-epoxy-1-butene, TS-1

## 1. Introduction

Isomorphous substitution of Si and/or Al atoms in ZSM-5 zeolite by titanium offered a new kind of catalyst, titanium silicalite-1 (TS-1), for the selective oxidation of organic chemicals [1]. The catalytic properties of TS-1 are of great interest, both scientifically and commercially, because the reactions catalyzed by TS-1 have the advantages of (1) mild reaction conditions (0–100 °C, ambient pressure), (2) being environmentally benign (by-product is $H_2O$), and (3) high activity and selectivity [2–4]. Several studies have been devoted to the synthesis, characterization, and catalytic application of titanium silicalite-1 molecular sieves [5–7]. TS-1 has been proved to catalyze a broad range of oxidation reactions with aqueous hydrogen peroxide, such as hydroxylation of aromatics [8,9], epoxidation of alkenes [10–12], ammoximation of cyclohexanone [13], and oxidation of alkanes [14,15] and alcohols [16–18]. The convenient and cost effective preparation, elucidation of catalytic mechanism, and new catalytic application of this catalyst were the highlight in recent years.

3,4-epoxy-1-butene (EPB) is an important intermediate with two functional groups (carbon–carbon double bond and oxirane), thus it exhibits the properties of both alkenes and epoxides. It can be converted to a variety of fine and special chemicals, such as 2-amino-3-butene-1-ol and 1-amino-3-butene-2-ol, 3,4-dihydroxy-1-butene, 2-halo-3,4-epoxy-1-butene, 2,3-dihydrofuran, and butylene carbonate. The conventional preparation of this compound was obtained by the hydrolysis of butadiene monochlorohydrin (1-chloro-3-butene-2-ol) in alkaline media, and the latter was synthesized by the oxidation of butadiene with hypochlorous acid [19]. This process involved several separation steps and produced various salts which were difficult to remove from the reaction solution and can be hazardous to the environment. Eastman's scientists developed a new and economical process [20] for the preparation of EPB by the gas-phase epoxidation of 1,3-butadiene by means of oxygen or oxygen-containing gases over silver-containing catalysts ($Ag/Al_2O_3$). However, the conversion of 1,3-butadiene in this process was limited, and the formation of higher oxidation products was inevitable. In this paper we report another process to prepare EPB catalyzed by TS-1 with hydrogen peroxide as the oxidant. The results demonstrate that the direct liquid-phase epoxidation of 1,3-butadiene with dilute hydrogen peroxide in the presence of TS-1 under mild conditions can produce EPB with high activity and selectivity. The mild reaction conditions and the usage of aqueous $H_2O_2$ as the oxidant provide a convenient and environmentally benign method for the preparation of EPB and the corresponding downstream products.

## 2. Experimental

### 2.1. Synthesis of TS-1

The synthesis of titanium silicalite-1 was carried out using tetrapropylammonium hydroxide (TPAOH, 1 M, prepared from tetrapropylammonium bromide in our laboratory) as template, tetraethylorthosilicate (TEOS), and tetrabutylorthotitanate (TBOT, dissolved in dry isopropyl alcohol) as silicon and titanium sources. The procedure was similar to the literature [1]. The thoroughly mixed TEOS and TBOT solution was introduced into the TPAOH solution dropwise at room temperature with vigorous stirring. The dropping speed was controlled carefully to avoid the appearance of white precipitate. The obtained clear so-

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lution was kept at room temperature for 60 min under magnetic stirring, then the temperature was raised to 75 °C to evaporate the ethanol. The mol composition of the precursor gel was 1TEOS : $x$TBOT : 0.35TPAOH : $40H_2O$, where $x = 0.01$, 0.013, 0.02, and 0.025, respectively. After reaction at 75 °C for 5 h, the precursor gel was transferred to a stainless-steel autoclave with PTFE liner and the crystallizing process was performed at 175 °C for 72 h. The final crystalline material was centrifuged, washed thoroughly with deionized water, air-dried overnight, and calcined at 550 °C for 5 h to remove the organic template.

### 2.2. Physicochemical characterization

X-ray powder diffraction (XRD) analyses were performed on a Rigaku D/Max 2400 X-ray diffractometer with Cu-K$\alpha$ radiation ($\lambda = 0.15418$ nm). Particle size was determined by using a JEM-1200 EX/S transmission electron microscope. Chemical analysis of TS-1 was done by ICP-AES on an ARL 3520 spectrometer. The samples were dissolved in hydrogen fluoride solutions. The FT-IR spectra of TS-1 with different titanium contents were recorded on a Nicolet 10 DX-FTIR spectrometer. Diffuse reflectance UV-Vis spectra were obtained on a Shimadzu UV-240 spectrometer with $BaSO_4$ as standard. The nitrogen adsorption/desorption isotherms were collected on a Micromeritics ASAP 2010 sorptometer. Before analysis, the sample was degassed at 423 K and $1.07 \times 10^{-3}$ KPa for 12 h.

### 2.3. Catalytic reactions

The oxidation reaction of butadiene was performed in a 100 ml stainless-steel autoclave with electrostatic stirrer. The designed amounts of catalysts were dispersed in 50 ml solvent, and $H_2O_2$ (30 wt%) was added into the autoclave, then the autoclave was compressed carefully. Introducing the butadiene gas through a needle valve started the reaction and the pressure was maintained at 0.15 MPa through the whole reaction process. After reaction for a certain period, evacuating out the gases through another needle valve terminated the reaction. The conversion of $H_2O_2$ was determined by standard iodometric titration. The products were analyzed on a Perkin–Elmer AutoSystem XL GC equipped with a capillary column (5% methylphenylsilicon, 40 m × 0.25 mm). The identification of different compounds was done by GC/FT-IR. All calculation results were based on hydrogen peroxide.

## 3. Results and discussion

### 3.1. Synthesis and characterization of TS-1

XRD patterns revealed that all samples contained MFI phase with good crystallinity and were consistent with the literature results [1]. TEM image revealed that the particle size of the prepared samples is about 100 nm (figure 1). Table 1 lists the physicochemical properties of TS-1 with various titanium contents. The Ti contents in the final crystalline material were similar to those introduced in the precursor gel. The incorporation of titanium in the framework position was confirmed by FT-IR spectra (figure 2). All samples exhibited a band at ca. 960 $cm^{-1}$, and its intensity increased upon the increasing of titanium contents. However, there were different opinions about the interpretation of the 960 $cm^{-1}$ band in the recently reported titanium-containing mesoporous molecular sieves (e.g., Ti-MCM-41

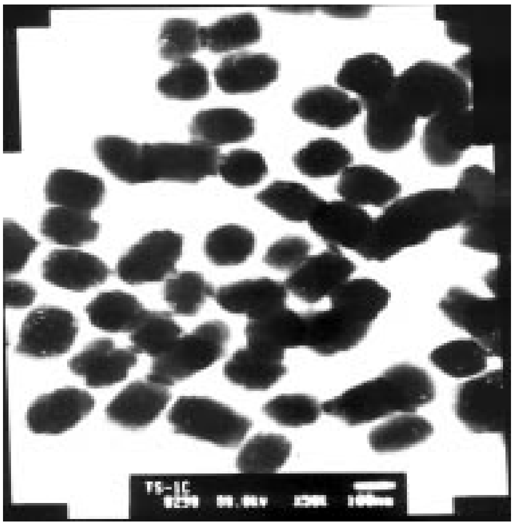


Figure 1. Representative TEM image of titanium silicate molecular sieve TS-1.

Table 1
Physicochemical properties of TS-1.

| Sample | $SiO_2/TiO_2$ Gel | $SiO_2/TiO_2$ Product | $S_{BET}$ ($m^2/g$) | Pore volume ($cm^3/g$) |
|---|---|---|---|---|
| TS-1(1) | 100 | 110 | 434.5 | 0.25 |
| TS-1(2) | 75 | 84 | 430.2 | 0.25 |
| TS-1(3) | 50 | 59 | 440.2 | 0.23 |
| TS-1(4) | 40 | 44 | 431.7 | 0.24 |

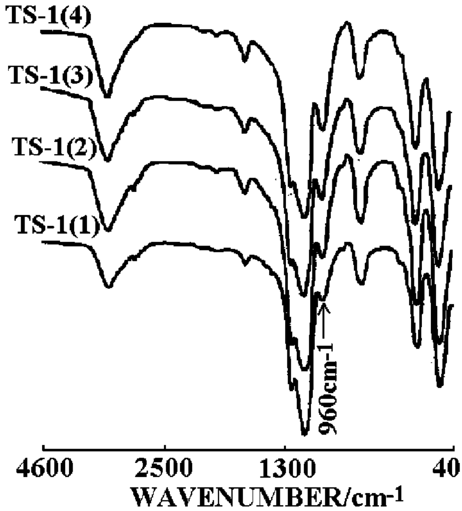


Figure 2. FT-IR spectra of TS-1 with different titanium contents.

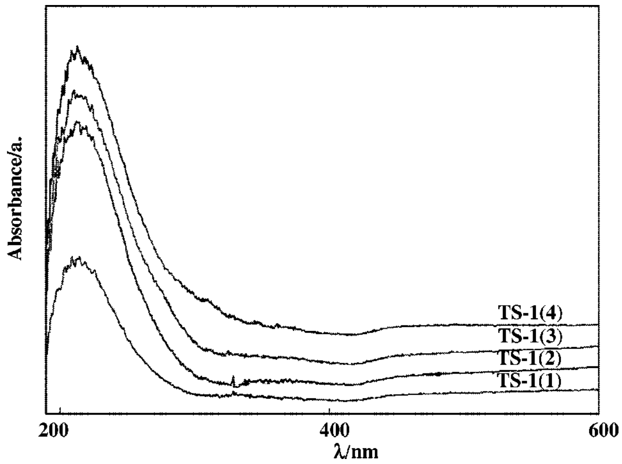


Figure 3. DR UV-Vis spectra of titanium silicate molecular sieves.

Table 2
The epoxidation performance of 1,3-butadiene over different catalysts.[a]

| Catalyst | Ti content (wt%) | $H_2O_2$ conversion (%) | TON[b] (mol 3,4-EPB/mol Ti) |
|---|---|---|---|
| Blank | – | 90.0 | n.d. |
| $SiO_2$ | 0 | 97.7 | n.d. |
| Silicalite-1 | 0 | 97.0 | n.d. |
| $TiO_2$ | – | 95.0 | n.d. |
| $SiO_2$–$TiO_2$ mixture[c] | 1.3 | 93.7 | n.d. |
| $TiO_2/SiO_2$[d] | 1.3 | 85.7 | n.d. |
| TS-1(3) | 1.3 | 99.0 | 193 |

[a] Reaction conditions: room temperature, 60 min, $CH_3OH$ 50 ml, catalyst 100 mg, $H_2O_2$ 0.23 M. All catalysts were calcined at 823 K for 5 h.

[b] n.d. = not detected.

[c] $SiO_2$–$TiO_2$ mixture was prepared by hydrolysis of TEOS and TBOT in a similar manner of preparation as of TS-1 but free of template.

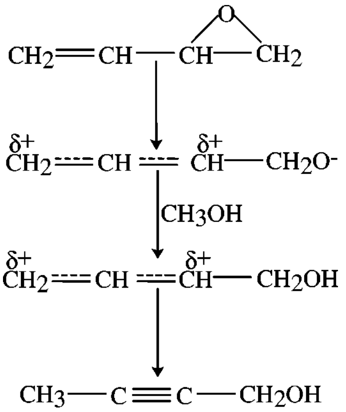
[d] $TiO_2/SiO_2$ was prepared by impregnation of TBOT in silica support.

and Ti-HMS). It has been believed extensively [4] to be a proof of titanium isomorphous substitution in the framework position of microporous molecular sieves, because it is absent in the spectrum of the corresponding titanium-free sample (silicate-1). The diffuse reflectance UV-Vis spectrosocopy is the most easily accessible method for direct probing of titanium environments in solids. The intensity of the adsorption peak at ca. 215 nm was slightly increased upon increasing the titanium content, as shown in figure 3. It is ascribed to the charge transfer spectra of Ti–O in tetrahedron environment [1]. The absence of the adsorption peaks above 330 nm suggested that the samples were free of extraframework titanium impurities [4].

### 3.2. Catalytic reaction

#### 3.2.1. Catalyst

Table 2 lists the catalytic results over TS-1 and other types of catalysts with similar titanium contents. All catalysts exhibited a very high activity towards to the conversion of $H_2O_2$. Silica-supported titania ($TiO_2/SiO_2$) and the $TiO_2$–$SiO_2$ mixture were reported [21] to be efficient catalysts for the epoxidation of olefins such as propene. In



Scheme 1.

the present study, however, GC analysis did not detect any organic products for these catalysts. The turnover number (TON, determined as the molar EPB obtained per molar Ti atom) and the concentration of EPB in the final reaction mixture were used to evaluate and compare the activities of different catalysts. It can be seen that EPB was only obtained when using TS-1 as the catalyst, and the TON reached to 193. This suggested that the titanium in the unique framework position of TS-1 was responsible for the high catalytic performance. The high hydrogen peroxide conversion over the other catalysts was the result of thermal and/or catalytic decomposition. Note that even in the blank reaction (without adding any catalysts), the conversion of $H_2O_2$ could reach to 90.0%. In the case of TS-1 as the catalyst, the oxidation of butadiene and the decomposition competed in the consumption of $H_2O_2$.

#### 3.2.2. Influence of temperature on activity and selectivity for the oxidation of butadiene

The experiments were performed at room temperature (25 °C) and 50 °C, respectively. When the catalytic oxidation was conducted at room temperature, only EPB was detected as the product, and the reaction selectivity to EPB was 100%. But when the reaction temperature was increased to 50 °C, the selectivity for EPB decreased to 60% and 2-butyn-1-ol was detected in GC analysis. Furthermore, the 2-butyn-1-ol was also observed when the reaction solution obtained at room temperature was reserved overnight. 2-butyn-1-ol is an isomer of 3,4-epoxy-1-butene, and it can be formed through the scheme 1. This process was thermodynamic related, and the increase of reaction temperature can increase the probability and speed of the isomerization reaction.

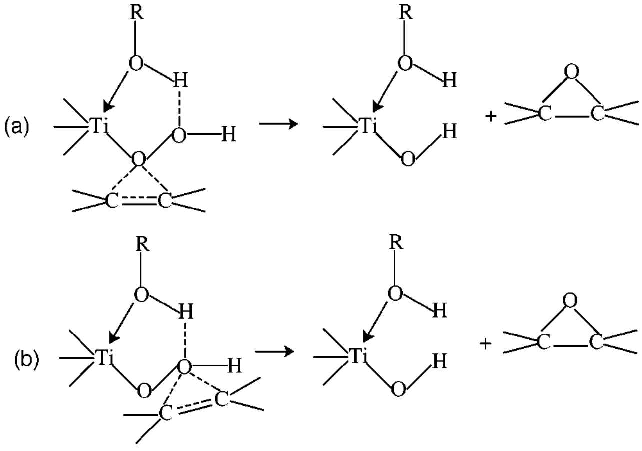
#### 3.2.3. Solvent effect on the performance of catalyst

The solvent effect on the monoepoxidation of butadiene is shown in table 3, where the conversion of $H_2O_2$ and the TON of 3,4-epoxy-1-butene are listed. The solvent effect on the performance of the catalyst was observed clearly. Although the $H_2O_2$ conversion was similar, the TON was significantly different in these solvents. Methanol was the best reaction medium for the epoxidation of buta-

Table 3
Solvent effects on the epoxidation of butadiene over TS-1.[a]

| Solvent | Reaction time (min) | $H_2O_2$ conversion (%) | TON (mol 3,4-epoxy-1-butene/ mol Ti) |
|---|---|---|---|
| $CH_3OH$ | 30 | 85 | 133 |
| $C_2H_5OH$ | 30 | 77.6 | 49 |
| $n$-$C_3H_7OH$ | 30 | 77.1 | 15 |
| $n$-$C_4H_9OH$ | 30 | 82 | n.d.[b] |

[a] Reaction conditions: solvent 50 ml, room temperature, $H_2O_2$ 0.23 M, TS-1(3) 100 mg.
[b] n.d. = not detected.



Scheme 2. From [4].

diene, whereas not any organic product was detected in butanol. According to the solubility principles, the solubility of butadiene in these solvents is increased in the following order: methanol < ethanol < propanol < butanol. Comparing this order with the catalytic results in table 3, it can be concluded that the dissolution of substrate in the solvent and the phase diffusion were not the determined factors for the epoxidation of butadiene in the presence of TS-1, i.e., the transfer of oxygen from the active intermediate to the butadiene was a fast reaction. A well-documented and widely accepted mechanism for the epoxidation of olefins over TS-1 is as given in scheme 2 [4]. It is the hydroperoxo species of titanium rather than its peroxo species that was responsible for the high selectivity and activity of TS-1 molecular sieves. The coordination of an alcohol molecule to the hydroperoxo species was necessary and important to stabilize the active sites. So the steric effects were critical in determining the stability of the five-member-ring intermediate. In addition, the increasing electrophilicity of the RO group (at the order of methanol < ethanol < propanol < butanol) decreased the stability of the intermediate. The small electrophilicity and steric constraints of methanol offered the best medium for the epoxidation of olefins.

### 3.2.4. *Influence of $H_2O_2$ concentration on activity and selectivity for the oxidation of butadiene*

The experiments were performed as described in section 2, only the concentration of hydrogen peroxide was changed. The concentrations of $H_2O_2$ were 0.226, 0.436, 0.630, 0.811, and 0.980 M, respectively. In figure 4 the TON is plotted against the hydrogen peroxide concentration. It can be found that the TON of 3,4-epoxy-1-butene increased linearly with increasing $H_2O_2$ concentration, and reached maximum when the concentration was 0.630 M. Further increasing of the hydrogen peroxide concentration led to the decreasing of the TON, and by-product was detected in GC analysis (not identified and quantified). This might be due to further oxidation of EPB.

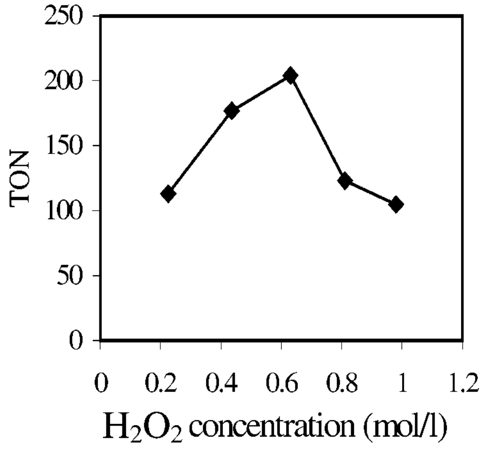


Figure 4. Effect of $H_2O_2$ concentration on the epoxidation of 1,3-butadiene. Reaction conditions: room temperature, time 60 min, TS-1(3) 100 mg, $CH_3OH$ 50 ml.

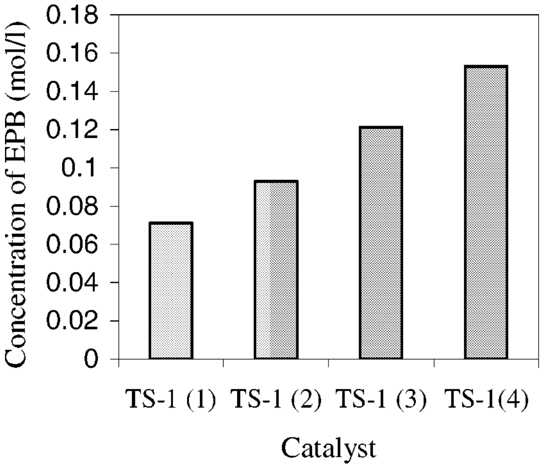


Figure 5. Effect of titanium content on the performance of the catalyst. Reaction conditions: room temperature, time 60 min, catalyst 100 mg, $CH_3OH$ 50 ml, $H_2O_2$ 0.23 M.

### 3.2.5. *The performance of catalyst with different titanium contents*

Figure 5 shows the results obtained in the epoxidation of butadiene over TS-1 with different titanium contents. The concentration of 3,4-epoxy-1-butene increased linearly upon increasing of the titanium content, suggesting it was titanium that actually acts as the active sites in TS-1. The high performance of TS-1 in the catalytic epoxidation of butadiene was closely related to the unique crystalline struc-

Table 4
Effect of TS-1 amounts and reaction time on the performance of butadiene epoxidation.[a]

| TS-1 amount (g/l) | Time (min) | $H_2O_2$ conversion (%) | 3,4-EPB concentration (mol/l) |
|---|---|---|---|
| 0 | 60 | 90 | n.d.[b] |
| 1.0 | 60 | 100 | 0.07 |
| 2.0 | 30 | 85 | 0.10 |
| 2.0 | 60 | 99 | 0.12 |
| 2.0 | 120 | 100 | 0.10 |
| 3.0 | 60 | 100 | 0.12 |

[a] Reaction conditions: $CH_3OH$ 50 ml, room temperature, $H_2O_2$ 0.23 M, catalyst TS-1(3).
[b] n.d. = not detected.

ture of TS-1 molecular sieves, i.e., the isolated titanium species in tetrahedron environments.

### *3.2.6. Influence of the amount of catalyst and reaction time*

Table 4 summarizes the amounts of 3,4-epoxy-1-butene obtained with different amounts of catalyst and reaction time. The product was not detected in the blank reaction (without adding catalyst). The maximum yield of 3,4-epoxy-1-butene was obtained when the amount of catalyst is 2.0 g/l and the reaction time is 60 min. This was due to the complete conversion of $H_2O_2$ under these conditions, and further increasing of the amount of catalyst and reaction time can cause side-reactions, thus does not lead to the increasing of the product amount.

## 4. Conclusions

- 1,3-butadiene can be catalytically epoxidated to 3,4-epoxy-1-butene selectively by hydrogen peroxide in liquid phase in the presence of TS-1 molecular sieve.
- 3,4-epoxy-1-butene was the only product when the reaction was conducted at room temperature (25 °C), and the increasing of temperature lead to the formation of other by-products.
- Methanol is the best solvent for the TS-1-catalyzed epoxidation of butadiene, and the optimum reaction conditions were 2.0 g/l catalyst, 0.63 M $H_2O_2$, and 60 min.

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