Epoxidation of Butadiene Over Nickel Modified TS-1 Catalyst

Mei Wu · Lingjun Chou · Huanling Song

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Abstract Nickel modified Titanium silicalite 1 (TS-1) catalysts provided an environmentally benign and effective method for butadiene epoxidation. Certain loading of modified Ni in our system significantly promoted TS-1 catalytic activity. The product vinyloxirane (VO) was obtained with high yield of 0.49 mol/L (theoretic equilibrium value 0.52 mol/L). The turnover number (TON, determined as the molar VO obtained per molar Ti atom) reached 1,140. Besides, the catalyst kept high activity during five runs of reusability test. XRD, N₂ adsorption and desorption, TPR, XPS, FT-IR and DR UV–Vis were employed to characterize the specific Ni role to Ti-site in Ni/TS-1 catalysts.

Keywords Butadiene · Epoxidation · Vinyloxirane · Titanium silicalite 1 · Nickel

1 Introduction

The epoxidation of butadiene (BD) is a typical atom economic reaction in respect of the activation of C=C bond [as shown in Eq. (1)]. The product vinyloxirane (VO) exhibits the characteristics of both alkenes and epoxides because of its two functional groups (carbon–carbon double bond and

M. Wu

Graduate School of Chinese Academy of Sciences, Beijing 100049, People's Republic of China oxirane) in one molecule, and thus shows great value as an intermediate in synthesizing organic chemistry and chemical technology [1]. A variety of fine and special chemicals such as 2-amino-3-butene-1-ol, butylenes carbonate etc. can be obtained from VO. Conventionally, VO is prepared by the hydrolysis of BD monochlorohydrin (1-chloro-3-butylene-2-ol) in alkaline media; BD monochlorohydrin is usually obtained through the oxidation of BD with hypochlorous acid [2]. This process has many disadvantages in regard of environmental and economic considerations.

In 1990s, Monnier prepared VO via the epoxidation of BD using oxygen or oxygen-containing gases as oxidant over silver catalysts (Ag/Al₂O₃), which made the synthesis of VO economical and environmental friendly [3]. Subsequently, a large number of investigations on Ag/Al₂O₃ system including catalysts and reaction mechanisms had been reported [1, 4–6]. In our previous work, the stability and activity of Ag/Al₂O₃ catalysts were greatly improved by IA/IIA metals [7]. However, the VO single-pass yield was relatively low, and deep oxidations of VO were inevitable at high temperature (>200 °C). Invention of titanium containing molecular sieves TS-1 by Taramasso et al. [8] opened a new route for catalytic reactions. For the unique pore-channel structure, TS-1 exhibits outstanding properties of shape selective catalysis oxidation. A lot of oxidation reactions with hydrogen peroxide (H_2O_2) as oxidant including alkenes epoxidation can be catalyzed by TS-1 [9–11]. Reactions over TS-1/H₂O₂ system, which can be performed under mild reaction conditions (0-100 °C,

M. Wu \cdot L. Chou \cdot H. Song (\boxtimes)

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China e-mail: songhl@licp.cas.cn

ambient pressure) with high activity and selectivity, are environmentally benign owing to H_2O as the only byproduct [12–14]. Therefore, TS-1 and H_2O_2 seem to construct optimum partners for the epoxidation of small alkenes. In 2000, TS-1/H₂O₂ system was applied to the liquid-phase epoxidation of BD. VO turnover number (TON, determined as the molar VO obtained per molar Ti atom) was 193 and VO concentration was 0.15 mol/L at optimal conditions, away from the theoretic equilibrium value (0.60 mol/L) [15].

Water soluble compounds of transition metals (e.g. sodium tungstate, molybdate and vanadate or potassium chromate and dichromate) have been used as homogeneous catalysts earlier in the epoxidation of olefinic compounds [16, 17]. Nevertheless, the process was inapplicable due to difficulties in the homogeneous catalysts separation/recycling. The simple, inexpensive metal oxides, such as NiO, CoO or MoO₃, were employed as heterogeneous catalysts for the epoxidation of styrene using tertiary butylhydroperoxide as an oxidant [18]; among these transition metal oxides, NiO showed the best performance (styrene conversion was 52 %, and styrene oxide selectivity reached 86 %). Although the problem of catalysts separation/ recycling has been solved, the activity of simple transition metal oxide for alkenes epoxidation still requires promotion.

The local environment of Ti studied in depth confirmed that titanium was in a tetrahedral environment in TS-1, and the type of species presenting as tetrapodal $[Ti(OSi)_4]$ and tripodal $[Ti(OSi)_3(OH)]$ were observed [19]. Consequently, a certain kind of acidity was introduced into the TS-1 catalyst. Although TS-1 exhibited remarkable selectivity, byproducts formed in the solvolysis of epoxides, which is catalyzed by the acid site on TS-1, are quite serious problems. Nowadays, alkali and alkaline-earth metals modified TS-1 catalysts were well studied to promote the selectivity of epoxides [20, 21]. However, the introduction of alkali and alkaline-earth metals suppresses the conversion of H₂O₂. Furthermore, the content of modified metal is difficult to control.

Based on the fact above, TS-1 exhibits attractive prospect for BD epoxidation due to its advantages in environmental benign and mild reaction condition. In recent years, the epoxidation of BD in liquid phase was studied rarely whatever using H_2O_2 or other oxidants. Herein, being inspired by the catalytic activity of simple transition metal oxide for alkenes epoxidation, we choose inexpensive transition metal Ni to modify TS-1, aiming to influence the electron environment of Ti active site and improve the electrophilicity of active oxygen in the five-member-ring intermediate. TS-1 catalysts modified with Ni were facilely prepared through supersonic impregnation method. The specific Ni role to Ti-site and the variation in the property of the active center towards the BD epoxidation reaction was investigated. The introduced Ni effectively improved VO yield and H_2O_2 utilization. The catalyst kept high activity during five runs of reusability test. In all, Ni modifying TS-1 catalysts provided an environmentally benign and effective method for BD epoxidation.

2 Experimental

2.1 Materials

Hydrogen peroxide (H₂O_{2,5} 0 wt%; local vender) concentrations were determined by iodometric titration prior to use. Titanium Silicalite 1 (TS-1, SiO₂/TiO₂ = 40) with specific surface area 463.1 m²/g was from Shanghai Novel Chemical Technology Co. Ltd. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Shanghai NO. 2 Reagent Factory, China) and methanol (CH₃OH, local vendor) employed were all A.R. grade. All chemicals were used without further purification.

2.2 Preparation of xNi-TS-1

The TS-1 catalysts with different Ni contents (denoted as xNi-TS-1, where x stands for NiO mass percent contents: $x = m_{NiO}/(m_{NiO} + m_{TS-1}) \times 100$, x range of 0–10) were prepared via supersonic impregnation method. This method facilitated Ni into TS-1 structure and potentiated the interaction between embedded Ni and Ti active site. The typical synthesis process was as follows: 1.00 g of TS-1 was dissolved in 3 mL distilled water, and then 5 mL distilled water containing designed amount of Ni(NO₃)₂·6H₂O was added into the above solution with vigorous stirring. The mixture was treated under ultrasonic wave, and then put into infrared drying oven with vigorous stirring until it changed to dry powder, finally further dried up overnight at 120 °C. The final powder in light green was calcined at 550 °C for 360 min. Chemical analysis of prepared catalysts was done by atomic absorption spectroscopy (ICP-AES) on an ARL 3520 spectrometer.

For comparation, the pure NiO particles were obtained by calcinating Ni(NO₃)₂·6H₂O at 450 °C for 3 h.

2.3 Physicochemical Characterization

2.3.1 Powder X-ray Diffraction (XRD)

XRD measurements were performed using an X'Pert Pro multipurpose diffractometer (PANalytical, Inc.) with Nifiltered Cu K α radiation (0.15046 nm) from 10.0° to 80.0°. Measurements were conducted using a voltage of 40 kV, current setting of 40 mA, step size of 0.02°, and count time of 4 s. Crystallite sizes of Ni particles were calculated using Scherrer' equation: $D_{(hkl)} = K\lambda/(\beta\cos\theta)$, where *K* was the shape factor of the average crystalline, λ was denoted as the wavelength (1.54056 Å for Cu K α), β was defined by a relationship between the full wave at half maximum (FWHM) of the sample and that of a quartz standard, and θ was the peak position.

2.3.2 N₂ Adsorption and Desorption

The N₂ adsorption and desorption isotherms at -196 °C were recorded on an Autosorb-iQ analyzer (Quantachrome Instruments U.S.). Prior to the tests, samples were degassed at 200 °C for 4 h. The specific surface areas were calculated via the BET method in the relative pressure range of 0.05–0.30; pore size distributions were calculated using adsorption branches of nitrogen adsorption–desorption isotherms by Saito–Foley (SF) methods.

2.3.3 H₂ Temperature Programmed Reduction (TPR)

H₂-TPR was performed on a Zeton-Altamira instrument (AMI-100) employing hydrogen as reducing agent. The samples (0.30 g) were loaded in a U-shaped quartz reactor. Prior to the TPR measurements, samples were pretreated at 400 °C for 30 min in flowing He (50 mL/min) to remove any moisture and other impurities that might be present. After cooling the reactor to 20 °C, a 5 % H₂–He (50 mL/min) gas mixture was introduced. And then the catalyst was heated to 900 °C at a rate of 20 °C/min and the hydrogen consumption was measured using an AMETEK (LC-D-200 Dycor AMETEK) mass spectrum.

2.3.4 X-ray Photoelectron Spectroscopy (XPS)

The oxidation state of titanium and nickel was characterized over a Thermo Fisher Scientific K-Alpha XPS. The xNiO-TS-1 powder was pressed to self-supporting wafer prior to analysis.

2.3.5 Fourier Transformed Infrared Spectra (FT-IR)

FT-IR of xNiO-TS-1 samples were recorded on FT-IR spectrometer (Nicolet Nexus 870) with a resolution of 4/cm and 64 scans in the region of 4,000–400/cm.

2.3.6 Diffuse Reflectance UV-Vis Spectra (DR UV-Vis)

The samples were dissolved in hydrogen fluoride solutions. DR UV–Vis was obtained on a Shimadzu UV-240 spectrometer with BaSO₄ as standard.

2.3.7 Thermogravimetric Analyzer (TGA)

TGA measurements were rendered on a NETZSCH STA 449F3 thermogravimetric analyzer from room temperature to 600 °C at the rate of 10 °C/min.

2.4 Catalytic Reactions

The epoxidation of BD was performed in a 100 mL stainless-steel autoclave with a magnetic stirrer. Typically, 0.40 g xNiO-TS-1 and designed amount of H₂O₂ was dispersed in 25.00 mL methanol solvent, and then the autoclave was compressed tightly. 0.15 MPa BD was introduced into the autoclave through a needle valve. The slurry was heated to 40 °C with vigorous stirring and kept at 40 °C for 60 min, and then quickly quenched in an ice water bath to around 0 °C. The remaining H₂O₂ concentration was determined by standard iodometric titration. The liquid products were confirmed by gas chromatography-mass spectroscopy (GC-MS 5973 equipment from Agilent Technology Company). VO was confirmed as the main products, and the main by-products were small amount of tetrahydro-2-furanmethanol and 4-ethenylcyclohexene. The quantity of products was performed on a gas chromatograph (SP-6800A GC) equipped with a flame ionization detector and OV-1701 capillary column. The VO yield was determined relating to methanol via external standard method based on the GC results, while the concentrations of by-products were too little to determine. The VO turnover number (TON, determined as the molar VO obtained per molar Ti atom) and the VO concentration of in the final reaction mixture were utilized to evaluate and compare the activities of different catalysts. The conversion and the utilization of H_2O_2 were calculated by Eqs. (2) and (3), respectively:

$$H_2O_2$$
utilization % = 100 × (n_{VO})] / [(nH_2O_2)_0 (3)

In above equations, the n_{VO} stands for moles of VO obtained from the epoxidation of BD; the $(nH_2O_2)_0$ and nH_2O_2 stand for the initial molar content and the remaining molar content of H_2O_2 after reaction, respectively.

3Ni-TS-1 was applied to determine the reusability of the catalyst for BD epoxidation. The first reaction was carried out as follows: 0.40 g catalyst, 0.15 MPa, 60 min, 40 °C, and 50 wt% H₂O₂ 0.52 mol/L, CH₃OH 25.00 mL. The catalyst after centrifugation was calcined at 450 °C for 180 min in muffle furnace and performed to the next reaction.

3 Results and Discussion

3.1 Characterization of Catalysts

3.1.1 XRD and N₂ Adsorption and Desorption Characterization

The XRD patterns of *x*Ni–TS-1 samples (x = 0, 3, 5, 10) were shown in Fig. 1A, they revealed that the structure of TS-1 with MFI phase [22] was undisturbed after Ni doped. However, as we can see from Fig. 1B, the diffraction angle of TS-1 skeleton structure shifted slightly from 23.56° (in TS-1) to 23.53° (in 10Ni–TS-1) with the Ni content increasing, which was corresponding to an increase of unit cell size because Si might be replaced by the Ni with larger size [23]. The small shift of diffraction angle indicated that



Fig. 1 A XRD patterns of various *x*Ni–TS-1 (x = 0, 3, 5, 10) catalysts. *a* TS-1, *b* 3Ni–TS-1, *c* 5Ni–TS-1, *d* 10Ni–TS-1 and **B** XRD patterns ($2\theta = 23.0^{\circ}-24.0^{\circ}$) of various *x*Ni–TS-1 (x = 0, 3, 5, 10) catalysts. *a* TS-1, *b* 3Ni–TS-1, *c* 5Ni–TS-1, *d* 10Ni–TS-1

the added Ni were probably embedded into the TS-1 framework as replacements of some Si sites, and had interaction with Ti active site in the TS-1 skeleton to some extent. Peak at $2\theta = 43.24^\circ$, assigned to NiO (JCPDS Card No. 87-0712), was hardly visible for 3Ni-TS-1 sample. It was difficult to calculate its crystallite size due to the diffraction peak broadening, demonstrating that the added Ni were embedded into carrier to form amorphous Ni species or the NiO particles maintained highly dispersed state, which were expected to give good yield to VO. The NiO phase peaks became intense as the Ni loading >5 wt%, illuminating that the grain size of NiO particles for the samples suffered significantly increase with increase of Ni loading. The average crystallite sizes of NiO particles calculated by the Scherrer equation were 127.50 nm in 10Ni-TS-1 and 78.24 nm in 5Ni-TS-1, respectively.

In order to observe clearly the influence of Ni on TS-1, we chose the representative xNi–TS-1 samples (x = 0, 3, 10) to determine N_2 adsorption properties and XPS analysis. The physicochemical properties of catalysts were summarized in Table 1. The BET surface area and total micropore volume of the samples slightly decreased from 463.1 to 437.9 m²/g and 0.175 to 0.165 cm³/g with the increase of Ni loading from 0 to 10 wt%, respectively. It suggested that some NiO particles blocked the pore channels of TS-1. Furthermore, when Ni loading increased to 10 wt%, the micropore volume of pore width between 0.457 nm and 1.00 nm decreased from 0.088 cm³/g to greatly 0.079 cm³/g. It can be explained that most of NiO particles located on the surface of the support owing to the larger Ni size. After reaction, the BET surface area and total micropore volume decreased greatly to less than 300.0 m²/g and 0.120 cm³/g, respectively. It was noteworthy that the micropore volume of pore width between 0.457 nm and 1.00 nm dropped from 0.088 to 0.019 cm^3/g for the used TS-1 sample. Compared with the fresh sample, it decreased 78 %, significantly higher than that of Nicontaining samples (about a decline of 40 %). The result demonstrated more organic macromolecules by-products were formed over TS-1, so as to clog the pore between 0.457 nm and 1.00 nm.

Table 1 Physicochemical properties of xNi–TS-1 (x = 0, 3, 10) obtained by BET method

Samples	BET st area (m ² /g)	BET surface area (m ² /g)		Micropore volume (cm ³ /g)		Micropore volume of pore between 0.457 and 1.00 nm (cm ³ /g)	
	Fresh	Used	Fresh	Used	Fresh	Used	
TS-1	463.1	293.57	0.175	0.114	0.088	0.019	
3Ni-TS-1	450.6	273.46	0.171	0.104	0.070	0.044	
10Ni-TS-1	437.9	248.20	0.165	0.096	0.079	0.046	

3.1.2 XPS Characterization

xNi-TS-1 (x = 3, 10) catalysts were analyzed by XPS in order to explore the oxidation state of nickel and titanium. The Ni²⁺ $2p_{3/2}$ XPS spectrum of free NiO usually shows peaks at 853.9 and 855.6 eV. While the Ni $2p_{3/2}$ XPS spectrum of samples showed peaks at 854.9, 856.3 eV (Fig. 2A). The increase of BE values indicated that Ni species in modified samples was afforded electrons by TS-1 support. The peak at 854.9 eV was attributed to Ni_{OC}^{2+} (Ni^{2+}) in an octahedral geometry), and the reducibility of Ni_{OC}^{2+} was greater than that of Ni_T^{2+} (Ni²⁺ in a tetrahedral geometry) [24, 25]. The peak at 856.3 eV was Ni_T^{2+} which was embedded in the TS-1 structure. The peak intensity at 856.3 eV was obviously enhanced with the increase of Ni content, indicating that the concentration of Ni species embedded in TS-1 support increased. However, the ratio of the peak intensity at 856.3 to 854.9 eV (Ni_T^{2+}/Ni_{OC}^{2+}) in



Fig. 2 A The Ni 2p XPS spectra of the xNi–TS-1 (x = 3, 10) sample. *a* 3Ni–TS-1, *b* 10Ni–TS-1. **B** The Ti 2p XPS spectra of the xNi–TS-1 (x = 0, 3, 10) sample. *a* TS-1, *b* 3Ni–TS-1, *c* 10Ni–TS-1

3Ni–TS-1 was larger than that in 10Ni–TS-1. It was suggested that the relative concentration of Ni interacting with the support was greater in the case of lower Ni loading.

The Ti $2p_{3/2}$ core-level spectra of the xNi–TS-1 (x = 0, 3, 10) samples were shown in Fig. 2B. It revealed that the characteristic spin-orbit splitting of titanium atoms in an oxide environment. The typical binding energy for Ti $2p_{3/2}$ in TS-1 is around 460.1 eV [26, 27]. While for the 3Ni-TS-1 sample, the binding energy of the most intense Ti $2p_{3/2}$ peak appeared at 459.3, 0.8 eV smaller than that of TS-1 reference sample. The decrease of binding energy suggested that Ti 2p core-level periphery electronic cloud density decreased. Combined with the Ni 2p XPS results, the change of Ti active site electronic environments was attributed to the embedded Ni. The electronic cloud of Ti active sites was drawn by Ni species, thus its periphery electronic cloud density decreased. In contrary, the peak at 460.1 eV of Ti $2p_{3/2}$ was preponderant for 10Ni–TS-1, but the peak at 459.3 eV, which was attributed to interaction between Ni and TS-1, was inferior. It demonstrated that the dominant Ti species in 10Ni-TS-1 were original from TS-1 framework. This was consistent with Ni $2p_{3/2}$ XPS spectrum above. It suggested that the interaction between embedded Ni and TS-1 skeleton varied with Ni loading. All binding energy were higher than that reported for octahedrally coordinated Ti(IV) with oxygen ions in TiO_2 [20, 28], suggesting free of extra framework titanium.

Surface Ni/Ti calculated from XPS relative atomic concentration and bulk Ni/Ti estimated using atomic absorption spectroscopy (ICP-AES) were studied. The surface Ni/Ti ratios for 3Ni–TS-1 (2.15:1) and 10Ni–TS-1 (4.63:1) proved to be higher than the bulk Ni/Ti ratios (0.64:1 for 3Ni–TS-1 and 1.76:1 for 10Ni–TS-1), indicating that some Ni atoms were probably incorporated into the TS-1 framework and others were dispersed on the surface of the support.

3.1.3 H₂-TPR Characterization

To better understand the interaction between Ni and TS-1, H₂-TPR was carried out in the range from 50 to 900 °C and the results were revealed in Fig. 3. The TPR study clearly demonstrated the differences in the interactions between Ni²⁺ and the support as varying Ni loading. For 3Ni–TS-1 sample, only one peak at around 500 °C was observed, which was assigned to embedded Ni species interacting with the support. This weak interaction decreased the reducibility of NiO and affected the electronic charge of Ti center, but did not change the TS-1 structure. In the case of Ni \geq 5 wt%, the additional region of higher temperature ranging from 650 to 800 °C appeared. It may be attributed to the formation of amorphous Ni silicate/titanium species, which were not visible in XRD, but enhanced the



Fig. 3 TPR profiles for xNi–TS-1(x = 3, 5, 10), ramping rate was 20 °C/min. *a* 3Ni–TS-1, *b* 5Ni–TS-1, *c* 10Ni–TS-1

interaction between Ni²⁺ and the support. The increasing peak intensity indicated that more Ni was embedded into the TS-1 framework with the increase of Ni content. However, the appearance of free NiO reduction peak (around 400 °C) was also observed due to higher Ni loading. The characterization results of TPR above were in good agreement with the XRD and XPS results.

3.1.4 FT-IR Spectra

The FT-IR spectra of TS-1 zeolite lattice vibration between 4,000 and 500/cm were depicted in Fig. 4a. The absorption bands at around 1100, 800 and 450/cm were lattice modes associated with internal linkages in [SiO₄] tetrahedral [29]. The absorption bands at around 1230 and 547/cm were characteristic peaks of the MFI type zeolite structure [30], which were consistent with the XRD characteristic MFI structure. The vibrational modes at around 970/cm are commonly believed to be the stretching mode of the $[SiO_4]$ tetrahedral bond with Ti atoms and the fingerprint of framework titanium [31-34]. Band shifting was observed after impregnation of Ni on TS-1. According to Fig. 4b, the wavenumber of titanyl [Ti-O] vibrations at 975.9/cm in TS-1 shifted down to 970.4/cm with the Ni loading increasing to 10 wt%, suggesting that the [Ti-O] bond weakened accounting for Ni incorporation. It might be ascribed to the charge transfer of [Ti-O] in tetrahedron environment. This feature suggested again that the added Ni changed the electronic charge of Ti center, which was in good agreement with the results above.

3.1.5 DR UV-Vis

To investigate the local environment of titanium and nickel in *x*Ni–TS-1 (x = 0, 3, 5, 10), samples were analyzed by



Fig. 4 FT-IR spectra of various xNi–TS-1 (x = 0, 3, 5, 10) catalysts. *a* TS-1, *b* 3Ni–TS-1, *c* 5Ni–TS-1, *d* 10Ni–TS-1

DR UV–Vis spectroscopy (as shown in Fig. 5). The adsorption peaks at 215 nm were ascribed to the charge transfer spectra of Ti–O in tetrahedron environment [8]. The absence of the adsorption peaks above 330 nm suggested that the samples were free of extra framework titanium impurities [3]. All samples showed an intense, asymmetric UV band with a maximum at 237 nm and a shoulder around 300 nm, which originated from $O \rightarrow Ni$ charge transitions of tetrahedrally coordinated Ni species incorporated into the TS-1 framework [35, 36]. Additionally, the weak d–d bands of octahedrally coordinated Ni²⁺ were also observed at 724 and 400 nm for 5Ni–TS-1 and 10Ni–TS-1[37], indicating that high loading of nickel resulted in formation of octahedral Ni species or NiO out of the framework. It was consistent with the XPS results.

The results of XRD, XPS, DR UV–Vis and TPR illustrated that parts of modified Ni were incorporated into the TS-1 skeleton as replacements of some Si sites and



Fig. 5 Diffuse reflectance UV–Vis (DR UV–Vis) spectra of TS-1 with different Ni contents. *a*TS-1, *b* 3Ni–TS-1, *c* 5Ni–TS-1, *d* 10Ni–TS-1

interacted with Ti active site. It might because ultrasoundassisted impregnation made the interaction between Ni and support stronger than conventional impregnation. These behaviors between the introduced Ni and TS-1 support resulted in the formation of a structure of NiO₄ coordinated with Ti and Si (structure 'a' as shown in Fig. 6), as similar as the case observed in Zn-treated TS-1[38]. Figure 6 was just schematic diagram which we supposed as the process of butadiene epoxidation catalyzed by Ni/TS-1. A welldocumented and widely accepted mechanism for the epoxidation of butadiene in TS-1/H₂O₂ system is as given A or B (as shown in Fig. 6) [14]. According to the FT-IR and XPS results, the periphery electronic cloud density of Ti active site reduced with Ni modifying, while the electrons around Ni species increased. It suggested the periphery electronic cloud around Ti center were attracted by embedded Ni. The reducing periphery electronic cloud density of the Ti center indicated its electrophilicity enhanced, and thus during the process of BD epoxidation, the electronic cloud of the O1 oxygen in intermediate A (or O2 in intermediate B) was easily attracted toward Ti center. Consequently, the electrophilicity of O1 in intermediate A (or O2 in intermediate B) was augmented, while the stability of the five-member-ring intermediate A (or B) decreased. Therefore, the double bond of BD can be easily oxidized by the O1 in intermediate A (or O2 in intermediate B).

3.2 Catalytic Activity

3.2.1 The Performance of Catalyst with Different Ni Contents

Figure 7 summarized the results of the BD epoxidation over TS-1 modified with different Ni contents. Specifically, when Ni loading was 0, H_2O_2 conversion was 98.8 %; H₂O₂ utilization and VO TON were 78.7 % and 952, respectively; and VO yield was 0.41 mol/L. With the increase of Ni content to 10 wt%, H₂O₂ conversion gave a slight decrease from 98.8 % over TS-1 to 94.7 %. Whereas, the maximum H₂O₂ utilization and VO TON with 98.3 % H₂O₂ conversion were obtained over 3Ni-TS-1 catalyst, which were 90.7 % and 1,140, respectively. At the same time, VO yield (0.49 mol/L) was very near to the theoretic equilibrium value (0.52 mo/L). In all, 3Ni-TS-1 catalyst exhibited the most excellent activity for BD epoxidation. Above characteristic results of xNi-TS-1 revealed reasons which could be responsible for its high catalytic performance. When Ni loading <3 wt%, less Ti active site was affected by the incorporated Ni, the modification effect was not that evident. For 3Ni-TS-1 sample, Ni species maintained highly dispersed state. Ni embedded in to TS-1 framework had appropriate interaction with the Ti active site. When Ni content ≥ 5 wt%, the formation of Ni silicate/titanium species from embedded Ni occupied the Ti center, Ni species on the external surface of TS-1 covered Ti active site and blocked the pore channel of TS-1, and thus depressed the catalytic activity. This could be confirmed by the BET and TPR results. To better understand the role of Ni, the pure NiO particles were used as catalyst to examine butadiene epoxidation under the same conditions. No VO product was obtained despite 30 % of H₂O₂ conversion. It implied that NiO was not as an active component for BD epoxidation. Furthermore, based on the reaction of the pure TS-1, the addition of Ni improved the H_2O_2 utilization or VO selectivity. Thus, Ni should be as a

Fig. 6 Scheme of five-memberring intermediate of BD epoxidation catalyzed by *x*Ni–TS-1





Fig. 7 Effect of Ni content on the BD epoxidation [Reaction conditions: 40 °C, 0.15 MPa, 60 min, H_2O_2 (50 wt%) 0.52 mol/L, xNi–TS-1 0.40 g, CH₃OH 25.00 mL]

promoter in Ni/TS-1 catalysts instead of synergistic role of titanium in BD epoxidation.

3.2.2 Influence of Reaction Time on BD Epoxidation

Figure 8 showed function of H_2O_2 conversion and VO concentration for epoxidation of BD as time on stream. The reaction had an extremely rapid start. In the initial 30 min, VO yield and H_2O_2 conversion increased linearly with the reaction time extending. As the reaction was performed at 40 °C for 30 min, we got the optimal results, VO of 0.50 mol/L was obtained (H_2O_2 conversion was 93.5 %). As time extending, even though H_2O_2 was still leveling off, there was hardly any more significant increase in VO concentration. It was implied that the epoxidation of BD reached the equilibrium quickly over Ni modified TS-1 catalyst in the initial 30 min. However, as time goes on, H_2O_2 and VO were consumed due to side reaction such as



Fig. 8 Effect of reaction time on the BD epoxidation (Reaction conditions: 40 °C, 0.15 MPa, H_2O_2 0.52 mol/L, 3Ni–TS-1 0.40 g, CH₃OH 25.00 mL)

further oxidation, solvolysis. Thus, the conversion of H_2O_2 increased, while the VO concentration decreased.

3.2.3 Influence of H₂O₂ Concentration on BD Epoxidation

Table 2 demonstrated the effect of H₂O₂ concentration on BD epoxidation reaction. Based on the reaction equation of BD and H₂O₂, the formation of one molecular VO would exhaust one molecular H2O2, and therefore theoretic equilibrium value of VO was corresponding to the initial H₂O₂ concentration. It can be seen that the conversion and utilization of H₂O₂ decreased slightly with the increase of H₂O₂ concentration, and the VO yield achieved theoretic equilibrium value when H₂O₂ concentration was lower than 0.52 mol/L. However, when H_2O_2 concentration increased over 0.52 mol/L, the H₂O₂ conversion and utilization decreased significantly. VO yield was far from the equilibrium yield, although it gave a biggish improvement from 0.61 mol/L in 0.78 mol/L H₂O₂ to 0.71 mol/L in 1.30 mol/L H₂O₂. For comparison, 30 wt% H₂O₂ was also employed, a slightly inferior results was obtained (VO yield was 0.46 mol/L; H₂O₂ conversion reached 95.3 %; H_2O_2 utilization was up to 87.5 %).

3.2.4 Reusability Tests of Catalysts

In this work, 3Ni-TS-1 was applied to explore the reusability of Ni modified TS-1 catalyst with repeated batch experiments. As shown in Fig. 9, the catalyst kept high activity during five runs, which provided 95.0 % H₂O₂ conversions and 0.48–0.42 mol/L VO yields, respectively. As observed in above characteristic patterns of 3Ni-TS-1, the good reusability was attributed to NiO particles which maintained highly dispersed state and appropriate interaction with the TS-1. A decrease of VO yield for the fifth repeated reaction was observed. On the one hand, due to the high activity of BD and VO molecules, self-polymerization

Table 2 Effect of H_2O_2 (50 wt%) concentration on the epoxidation of BD. (Reaction conditions: 40 °C, 60 min, 0.15 MPa, 3Ni–TS-1 0.40 g, CH₃OH 25.00 mL.)

CH ₂ O ₂ (mol/L)	H ₂ O ₂ conv. (%)	H ₂ O ₂ utilization (%)	VO yield (mol/L)	
0.26	99.7	96.0	0.26	
0.39	99.3	97.3	0.39	
0.52	98.3	91.9	0.49	
0.52 ^a	95.2	87.5	0.46	
0.78	82.0	76.1	0.61	
1.04	70.2	63.2	0.67	
1.30	64.1	54.4	0.71	

^a H₂O₂ (30 wt%)



Fig. 9 Reusability tests of catalysts. [Reaction conditions: 40 °C, 0.15 MPa, 60 min, H_2O_2 (50 wt%) 0.52 mol/L, 3Ni–TS-1 0.40 g, CH₃OH 25.00 mL]



Fig. 10 TGA patterns of 3Ni-TS-1 after five runs

can occur easily. Those organic macromolecules could deposit in the TS-1 pore channel and overlay Ti active sites. On the other hand, the average pore diameter of 0.55 nm for TS-1 catalyst is very close to BD molecular size (0.55 nm). Once the side reaction (e.g. polymerization, oxidation, solvation etc.) occurred, the byproduct molecules with larger size could hardly escape from the pore. Indeed, the TGA analysis (Fig. 10) of the used catalyst after five runs clearly showed an exothermic peak at around 425 °C, which was assigned to the organic compounds decomposition burning. However, the weight loss of 1.95 wt% suggested these concomitant reactions and undesirable products were acceptable to some extent.

4 Conclusions

In summary, TS-1 zeolite modified with Ni (xNi–TS-1) effectively catalyzed epoxidation of BD under mild reaction condition using H₂O₂ as oxidant. TS-1 remained MFI

structure even Ni content up to 10 wt%. However, optimum reaction results were obtained over 3Ni-TS-1 catalyst, such as 1140 of VO TON, 0.49 mol/L of VO yield near to theoretic equilibrium value, over 98 % of H_2O_2 conversion and 91 % of H₂O₂ utilization. As we can see from various characterizations of catalysts, excellent dispersion of NiO particles and the appropriate interaction of Ni with TS-1 support must be responsible for this outstanding performance. The introduced Ni into TS-1 coordinated with Ti through NiO₄, changed the electronic environment of Ti center, enhanced the electrophilicity of the active oxygen, and thus improved the catalytic activity of TS-1 greatly. In addition, xNi-TS-1 catalyst exhibited good reusability for BD epoxidation. For these favorable advantages, TS-1 catalyst modified by Ni is a promising candidate for liquid phase epoxidation of BD.

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