

Tandem Lewis acid catalysis for the conversion of alkenes to 1,2-diols in the confined space of bifunctional TiSn-Beta zeolite

Qifeng Lei^a, Chang Wang^a, Weili Dai^{a,*}, Guangjun Wu^a, Naijia Guan^{a,b}, Michael Hunger^c, Landong Li^{a,b}

^a School of Materials Science and Engineering & National Institute for Advanced Materials, Nankai University, Tianjin 300350, China

b Key Laboratory of Advanced Energy Materials Chemistry of the Ministry of Education, Collaborative Innovation Center of Chemical Science and

Engineering, Nankai University, Tianjin 300071, China

^cInstitute of Chemical Technology, University of Stuttgart, Stuttgart 70550, Germany

ARTICLE INFO

Article

Article history: Received 22 September 2020 Accepted 2 November 2020 Available online 5 March 2021

Keywords: Tandem catalysis Confinement effect Zeolite Alkene epoxidation Epoxide hydration

1. Introduction

ABSTRACT

The generation of multifunctional isolated active sites in zeolite supports is an attractive method for integrating multistep sequential reactions into a single-pass tandem catalytic reaction. In this study, bifunctional TiSn-Beta zeolite was prepared by a simple and scalable post-synthesis approach, and it was utilized as an efficient heterogeneous catalyst for the tandem conversion of alkenes to 1,2-diols. The isolated Ti and Sn Lewis acid sites within the TiSn-Beta zeolite can efficiently integrate alkene epoxidation and epoxide hydration in tandem in a zeolite microreactor to achieve one-step conversion of alkenes to 1,2-diols with a high selectivity of >90%. Zeolite confinement effects result in high tandem rates of alkene epoxidation and epoxide hydration as well as high selectivity toward the desired product. Further, the novel method demonstrated herein can be employed to other tandem catalytic reactions for sustainable chemical production.

© 2021, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

1,2-Diols, mainly produced by epoxide hydration, are extensively utilized as intermediates for producing chemical products such as antifreezes and polyester resins, medicines, and cosmetics [1]. Thus far, a variety of acidic and basic catalysts, including cation- and anion-exchange resins [2,3], supported metal oxides [4,5], amines [6], and silica-based reagents for nanoreactors [7,8], have been utilized in epoxide hydration. Previously, we reported the excellent catalytic performance of Lewis acidic Sn-containing zeolites in epoxide hydration [9,10]. As well-known carbon electrophiles, epoxides are mainly produced from corresponding alkene the precursors.

Ti(IV)-containing zeolites, such as Ti-Beta and TS-1, have been successfully utilized as efficient catalysts for alkene epoxidation with hydrogen peroxide [11–13]. Therefore, theoretically, 1,2-diols can be produced by alkene epoxidation using an appropriate oxidant over Ti-containing zeolites, followed by epoxide hydration over Sn-containing zeolites (Fig. 1, Route a). Although desirable activity can be achieved in both alkene epoxidation and epoxide hydration over Ti- and Sn-containing zeolite catalysts, respectively, the development of novel routes for the one-step conversion of alkene to 1,2-diols with high selectivity can be highly effective for decreasing the separation cost and achieving high energy utilization efficiency.

Tandem catalysis, which integrates multistep sequential re-

^{*} Corresponding author. Tel/Fax: +86-22-85358536; E-mail: weilidai@nankai.edu.cn

This work was supported by Municipal Natural Science Foundation of Tianjin (18JCJQJC47400, 18JCZDJC37400) and the Fundamental Research Funds for the Central Universities.

DOI: 10.1016/S1872-2067(20)63734-2 | http://www.sciencedirect.com/journal/chinese-journal-of-catalysis | Chin. J. Catal., Vol. 42, No. 7, July 2021



Fig. 1. Routes for the conversion of alkenes to 1,2-diols. Route a: indirect route including two processes: alkene epoxidation and epoxide hydration. Route b: tandem catalytic route of this study.

actions into a single-pass reaction, provides opportunities to develop new and efficient catalytic routes [14-22]. Various types of active sites are required to combine individual steps into a tandem catalysis reaction. In addition, to achieve high catalytic efficiency in tandem reactions, the types and distributions of the active sites should be controlled for individual reactions, and the reaction conditions should be balanced [23,24]. Lewis acidic zeolites are generally obtained by incorporating heteroatoms into the zeolite framework via direct hydrothermal synthesis or post synthesis, and several monometallic zeolite catalysts, such as Ti-Beta, Sn-Beta, Zr-Beta, Ta-Beta, etc. [25-29], have been shown to exhibit desirable catalytic performance in numerous reactions. However, for certain tandem reactions, it is of significant importance to obtain a large number of different types of isolated Lewis acid sites within the zeolite structure. Li et al. [30] directly synthesized ethylene glycol (EG) from ethylene over Al-TS-1 zeolite, but with a low EG selectivity of \sim 35%. Recently, Wu et al. [31] reported that Ti-MWW exhibited desirable catalytic activity toward ethylene to EG conversion.

Herein, for the first time, we introduce tandem catalysis for the direct transformation of alkenes to 1,2-diols by developing isolated dual Lewis acid sites within the zeolite structure as molecular reactors (Fig. 1, Route (b)). We demonstrate that bifunctional TiSn-Beta zeolite with isolated Lewis acid Ti and Sn sites obtained using a simple and scalable post-synthesis route can efficiently integrate alkene epoxidation and epoxide hydration in tandem in one reactor to achieve high selectivity (>90%) for 1,2-diols. The method of Lewis acid tandem catalysis in zeolite cages presented in this study can be applied for other tandem catalytic processes for sustainable chemical production.

2. Experimental

2.1. Preparation of zeolite catalysts

Ti- and/or Sn-containing Beta zeolites were prepared via a two-step post-synthesis procedure, as described elsewhere [9,10], which involves the dealumination of parent H-Beta zeo-

lites and the subsequent introduction of Sn species into the dealumination [Si]Beta zeolite. The obtained samples were denoted as Ti-Beta, Sn-Beta, and TiSn-Beta, and the quantity of Ti or Sn was 5 wt%, unless otherwise specified. Further, Ti-Sn-Beta and Sn-Ti-Beta zeolites were prepared using the same method as that used for preparing TiSn-Beta zeolite, but with different introduction sequences of the Ti and Sn species (TiSn-Beta: Ti and Sn were co-introduced; Ti-Sn-Beta: Ti was first introduced, followed by Sn; Sn-Ti-Beta: Sn was first introduced, followed by Ti). Full details of the sample preparation are provided in the Supporting Information.

2.2. Characterization techniques

The physicochemical properties of the as-prepared samples were characterized by X-ray diffraction (XRD), nitrogen adsorption, transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HR-TEM). The precise weight loadings of Sn and/or Ti species were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The changes in the hydroxyl groups in the H-Beta, dealumination [Si]Beta, and Ti- and/or Sn-containing beta samples were investigated by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The chemical environment and the nature of the Sn and Ti species within the [Si]Beta zeolite were verified by diffuse reflectance ultraviolet-visible (UV-vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), and solid-state ¹¹⁹Sn magic-angle spinning (MAS) NMR spectroscopy. The Lewis acidic character of Ti and/or Sn sites in Ti- and/or Sn-containing Beta samples was qualitatively and quantitatively identified using trimethylphosphine oxide (TMPO) and NH₃ adsorption and studied by ³¹P and ¹H MAS NMR spectroscopy, respectively. Further equipment parameters and the experimental details of the abovementioned characterization are provided in the Supporting Information.

2.3. Catalytic performance evaluation

The catalytic performance was tested in a Teflon-lined stainless-steel autoclave. Typically, 5 mmol alkene, 5 mmol H_2O_2 (31 wt% aqueous solution), 2.5 mL of solvent, and 0.1 g of the catalyst were added into the autoclave and mixed vigorously using a magnetic stirrer. Subsequently, the autoclave was heated to the desired reaction temperature and maintained for a certain duration of time at a stirring rate of 500 rpm. After the reaction, the products were analyzed using a Shimadzu gas chromatography-mass spectrometry (GC-MS) QP2010 SE and quantitatively determined using a Shimadzu 2010 GC equipped with an Agilent HP-5MS column (30 m × 0.25 mm × 0.25 µm), with the use of chlorobenzene as an internal standard. A carbon balance of approximately 95% was achieved during all the experiments.

3. Results and discussion

3.1. Design of zeolite samples and structural characterization

Table 1Physicochemical properties of the samples under study.

Samples	Si/Al Ti loading ^a Sn loading ^a Surface area ^b Pore volu				
	ratio ^a	(wt%)	(wt%)	(m²/g)	(cm ³ /g)
H-Beta	13.5	_	_	590	0.204
Si-Beta	>1800	_	_	620	0.210
Ti-Beta	>1800	4.8	_	598	0.199
Sn-/Beta	>1800	_	4.9	605	0.201
TiSn-Beta	>1800	4.6	4.7	588	0.192
TiSn-Beta d	>1800	4.5	4.7	580	0.191

^a Determined by ICP.^b Obtained using the BET method. ^cCalculated from the t-plot. ^dSample obtained after four reaction cycles.

Experimentally, Ti- and/or Sn-containing beta zeolites were fabricated using a two-step post-synthesis approach. First, de-aluminated [Si]Beta zeolites were prepared using the nitric acid treatment of H-Beta zeolites. Subsequently, Ti- and/or Sn-Beta zeolites were prepared by the introduction of Sn and/or Ti precursors into the [Si]Beta zeolites [9,10]. The possible textural property changes during the post-synthesis of zeolites were studied by XRD, DRIFT, and solid-state NMR. Typical diffraction patterns of beta zeolites were observed for all the samples, which revealed that the structure of the beta zeolite was well preserved during the post-synthesis process; these results are consistent with those reported previously [9,10]. The textural properties of the beta zeolites utilized in this study are presented in Table 1. No distinct changes in the BET areas and micropore volumes occurred after de-alumination and Sn and/or Ti introduction. This result implies that the characteristics of the beta zeolites were not influenced by the introduction of Sn and/or Ti. In addition, distinct diffraction lines owing to the Ti and/or Sn species were observed for the Ti- and/or Sn-containing zeolites (Fig. 2(a)). According to the ICP results (Table 1), 4.5 wt%-4.9 wt% loadings of Ti or Sn can be achieved. This result indicates that a high dispersion of the Ti and/or Sn species can be obtained using the Ti- and/or Sn-containing zeolites, which was consistent with the TEM results.

The DRIFT spectra of the zeolite samples are shown in Fig.



Fig. 3. ²⁹Si MAS NMR spectra of the as-prepared samples under study.

2(b). After dealumination, the Si-OH-Al group (3600 cm⁻¹) of H-Beta disappeared. Moreover, the bands at 3735 and 3520 cm⁻¹ assigned to internal SiOH and the hydrogen-bonded Si-OH groups, respectively, appeared for the [Si]Beta zeolite, indicating the formation of vacant T sites [9,10,32]. After the introduction of the Ti and/or Sn species, a significant decrease was observed in the intensity of the Si-OH groups at 3735 (shift to 3740 cm⁻¹) and 3520 cm⁻¹, indicating the interactions of the Ti and/or Sn species with silanol groups from de-alumination. The ²⁹Si MAS NMR spectra of the [Si]Beta and Ti- and/or Sn-containing beta samples indicated numerous similar signals at -103, -113 and -116 ppm (Fig. 3). The signal at -103 ppm was due to the Q3 species (Si-OH), while the signals at -113 and -116 ppm were assigned to the Q4 species at different sites. After the introduction of the Ti or Sn species into the [Si]Beta zeolite, a significant decrease in the Q3 signal (SiOH) intensity was observed, indicating an interaction between the Ti and/or Sn species with SiOH and the formation of the Si-O-Ti or Si-O-Sn bonds.

The distribution of the Ti and/or Sn sites in the [Si]Beta matrix was further studied by electron microscopy. The bright-field HRTEM image of the TiSn-Beta sample exhibited clear lattice fringes of the zeolite matrix; however, there was no



Fig. 2. (a) XRD patterns of the samples; (b) DRIFT spectra of the samples in the hydroxyl stretching vibration region.



Fig. 4. (a) HAADF-STEM images with the corresponding element mapping of TiSn-Beta zeolite; Ti 2*p* (b) and Sn 3*d* (c) XPS of Ti- and Sn- containing samples.

clear evidence of the Ti-Sn species in the zeolite (Fig. S1). In addition, a homogeneous distribution of the Ti and Sn species and their partial close contact can be observed based on the element mapping results (Fig. 4(a)).

The existing states of the Ti and/or Sn species were analyzed by XPS. As shown in Fig. 4(b), the binding energies of 460.1 and 465.7 eV ascribed to Ti $2p_{3/2}$ and $2p_{1/2}$, respectively, were observed for Ti-Beta and TiSn-Beta. These values were significantly higher than those of bulk TiO₂ (458.4 and 464.2 eV) because of Si–O–Ti bond formation. Similarly, the binding energies of 487.8 and 496.2 eV corresponding to Sn $2p_{3/2}$ and $2p_{1/2}$ higher than those of bulk SnO₂ (486.0 and 494.5 eV) were observed for the Sn-Beta and TiSn-Beta samples (Fig. 4(c)). As reported previously [9,10,33], the higher binding energies of the Ti and Sn atoms in the zeolites than those of the corresponding bulk oxides indicate the possible formation of tetrahedrally coordinated Ti(IV) and Sn(IV) species; however, it requires further investigation.

Further, UV-vis and 119Sn MAS NMR spectroscopy were employed to investigate the nature of the Ti and/or Sn species in the beta zeolite framework. As shown in Fig. 5(a), the dehydrated Ti-Beta zeolite exhibited a dominant UV-vis absorption band at approximately 218 nm. According to the previous studies [12,34,35], this band could be due to the framework Ti species with tetrahedral coordination. The Sn-Beta sample exhibited a sharp absorption band centered at approximately 207 nm, which is attributed to the tetrahedrally coordinated Sn species in the zeolite framework [36,37]. In addition, a strong UV-vis band centered at approximately 207 nm with a large shoulder at approximately 218 nm appeared for the TiSn-Beta zeolite. These bands were assigned to the tetrahedrally coordinated Ti and Sn species in the beta zeolite framework, respectively. These results indicated that the Ti and Sn species in the dehydrated TiSn-Beta zeolite mainly existed in tetrahedral coordination within the zeolite framework; these results are in accordance with the results from XPS analyses. As shown in Fig. 5(b), a significantly distinct ¹¹⁹Sn MAS NMR signal at -443 ppm appeared for the dehydrated Sn-Beta and TiSn-Beta zeolites. Based on the previous studies [38], these signals were assigned

to the framework Sn species with tetrahedral coordination and in a closed arrangement. In addition, the ¹¹⁹Sn MAS NMR signal at -420 ppm indicated that few Sn species with tetrahedral coordination but with an open arrangement might be present; however, this signal was overlapped by the broad signal at -443 ppm. Upon hydration, these signals disappeared; however, new signals appeared at -689 ppm, corresponding to the Sn sites octahedrally coordinated with water molecules [38,39]. Additionally, ¹¹⁹Sn MAS NMR signals ($\delta_{119Sn} = -605$ ppm) attributed to bulk SnO₂ appeared neither for dehydrated nor



Fig. 5. (a) UV-vis spectra of the dehydrated samples; (b) ¹¹⁹Sn MAS NMR spectra of the Sn-Beta and TiSn-Beta samples before and after hydration; (c) ¹H MAS NMR spectra of the dehydrated samples before (top) and after (middle) ammonia loading. The difference spectra (bottom) were obtained by subtracting the top spectra from the middle spectra; (d) ³¹P MAS NMR spectra of TMPO-loaded samples.

hydrated Sn-Beta and TiSn-Beta samples, excluding the formation of extra-framework SnO_2 species. Based on these experimental results, we concluded that most of the Ti and Sn species are incorporated into the beta zeolite framework and exist in a highly isolated state in the TiSn-Beta zeolite obtained from post-synthesis modification.

Further, the hydroxyl groups in the Ti- and Sn-containing beta samples were studied by ¹H MAS NMR spectroscopy. As shown in Fig. 5(c), a high-intensity ¹H MAS NMR signal in the range 1.3-1.6 ppm, attributed to the Si-OH groups, appeared for all the samples. Upon ammonia loading, additional ¹H MAS NMR signals were not observed in any of the samples. However, the intensities of the 1H MAS NMR signals at 1.3-3.0 ppm were enhanced after ammonia loading. According to the previous studies [40-42], the enhanced ¹H MAS NMR signals are due to Lewis acid sites coordinated with the ammonia probe molecules. In addition, no Brønsted acid sites that could produce ammonium ions (δ_{1H} = 6–7 ppm) after ammonia protonation were observed. These results reveal that only Lewis acid sites are formed after introducing Ti and/or Sn species into the [Si]Beta matrix. The densities of the strong Lewis acid sites, as evaluated based on the intensities of the 1H MAS NMR signals at 1.3–3.0 ppm, were 0.25, 0.13, and 0.36 mmol/g for the Ti-Beta, Sn-Beta, and TiSn-Beta samples, respectively. The results indicated that the amount of Lewis acid sites in the TiSn-Beta zeolite was close to the sum of the amounts of acid sites available in the Ti-Beta and Sn-Beta zeolites, thereby revealing the successful preparation of TiSn-Beta zeolite. As further proof of the formation of Lewis acid sites in the Ti-Beta, Sn-Beta and TiSn-Beta samples under study, the ³¹P MAS NMR spectra of the dehydrated samples loaded with TMPO probe molecules were examined. As shown in Fig. 5(d), a strong signal at δ_{1P} = 41 ppm ascribed to the TMPO molecules adsorbed on the weak acidic Si-OH groups appeared for all the samples. Additional ³¹P MAS NMR signals at 52-54 ppm attributed to the TMPO molecules coordinated with the Lewis acid sites appeared [42]; this result is consistent with the ¹H MAS NMR results.

3.2. Catalytic performance and stability

The catalytic performance of the as-prepared zeolites was examined for the direct conversion of cyclohexene to 1,2-cyclohexanediol using hydrogen peroxide solution (i.e., H₂O₂), which functions as an oxidant, for alkene epoxidation as well as the nucleophile (i.e., H₂O) for epoxide hydration. As shown in Fig. 6(a), almost no products could be observed over Sn-Beta zeolite, indicating that Sn-Beta is inactive in the conversion of cyclohexene to 1,2-cyclohexanediol. In contrast, considerable cyclohexene conversion with different product distributions could be obtained over Ti-containing beta zeolite catalysts (i.e., Ti-Beta, Ti- and Sn-Beta, Ti-Sn-Beta, Sn-Ti-Beta, and TiSn-Beta). For Ti-Beta zeolite, a high epoxide yield with a low amount of 1,2-diols could be achieved, indicating that Ti species are beneficial for alkene epoxidation; this result is consistent with the results in previous studies [31]. Additionally, the corresponding catalytic performance of the mixed Ti-Beta and Sn-Beta zeolites was evaluated for comparison. A significant decrease in the epoxide yield with an increase in the 1,2-diol yield was observed, indicating that the sequential reactions of alkene epoxidation and epoxide hydration were achieved to a certain extent in the presence of Sn-Beta. Moreover, it was revealed that the Lewis acidic Sn species are the main active sites for epoxide hydration, and this result is also supported by the results of cyclohexene oxide hydration (Fig. S2). However, a large number of by-products originating from the self-condensation of 1,2-diol or the excessively oxidized species, as shown in Fig. 6(a), were also obtained over the mixed catalysts simultaneously. For the bifunctional Ti- and Sn-containing beta zeolites, TiSn-Beta, 1,2-diol was observed to be the main product, indicating that the close distance between the two functional sites in the confined space of the zeolite leads to its desirable activity [43]. Therefore, the tandem catalysis of cyclohexene to 1,2-cyclohexanediol can be efficiently achieved in the confined cages of the TiSn-Beta zeolite.

Moreover, the introduction sequences of the Ti and Sn species were observed to exhibit a significant influence on their catalytic activity. TiSn-Beta zeolite with the co-introduction of the Ti and Sn species exhibited the highest catalytic performance, while Ti-Sn-Beta and Sn-Ti-Beta zeolites with the stepwise introduction of the Ti and Sn species exhibited relatively low catalytic activities (Fig. 6(a)). This can be explained by the formation of inert extra-framework SnO2 or TiO2 species during stepwise introduction, as shown in the UV-vis results (Fig. S3). These results confirm that co-introduction ensures the formation of isolated, tetrahedrally coordinated Ti and Sn sites in the zeolite framework, while stepwise introduction leads to the extra-framework oxide formation of the second element, the SnO₂ or TiO₂ species, which was significantly less active in the conversion of cyclohexene to 1,2-cyclohexanediol. To investigate the effect of the catalyst support on the performance of the TiSn-loaded catalysts in the conversion of cyclohexene to 1,2-cyclohexanediol, we prepared the $TiSn-SiO_2$ and TiSn-SBA-15 catalysts and compared their catalytic activities with that of the TiSn-Beta catalyst (Fig. S4). The results clearly indicate that the supports exhibited a strong impact on the performance of the TiSn-modified catalysts during the conversion of cyclohexene to 1,2-cyclohexanediol. Because TiSn-SBA-15 and TiSn-SiO₂ possess large pore windows but do not possess confined cages, the cyclohexene molecules can easily diffuse out of the catalyst; therefore, they exhibit significantly lower catalytic activity. With TiSn-Beta, the cyclohexene molecules can be subjected to diffusion resistance within the zeolite channels or cages, which can significantly improve cyclohexene conversion.

Owing to its outstanding activity, the bifunctional TiSn-Beta is regarded as a promising solid catalyst for the direct conversion of alkene to 1,2-diol. Further, the effects of the reaction parameters on the catalytic activity of TiSn-Beta zeolite were examined (Table S1, Figs. 6(b,c)). Table S1 presents the effects of solvents on the catalytic activity of TiSn-Beta catalysts in the direct conversion of cyclohexene to 1,2-cyclohexanediol. Aprotic solvents, such as acetone, 1,4-dioxane, and γ -valerolactone, with the lone pairs of electrons are beneficial for the formation of 1,2-diols with acetone being the most suitable. Further, the



Fig. 6. (a) Product yields over the different catalysts (TiSn-Beta: Ti and Sn were co-introduced; Ti-Sn-Beta: Ti was first introduced followed by Sn; Sn-Ti-Beta: Sn was first introduced followed by Ti). (b) Product yields during cyclohexene conversion over TiSn-Beta zeolite with different Ti and Sn weight loadings (2.5%;7.5%, 5%;5%, and 7.5%;7.5%). (c) Effect of reaction temperature on cyclohexene conversion and 1,2-cyclohexanediol selectivity catalyzed by TiSn-Beta zeolite. (d) Cyclohexene conversion and diol selectivity during cyclohexene conversion over TiSn-Beta zeolite, plotted as a function of time-on-stream. Reaction conditions: 5 mmol cyclohexene; 2.5 mL of MeCN ((a) and (b)), MeCOMe ((c) and (d)); 5 mmol H₂O₂; 0.1 g of catalyst; temperature 333 K ((a), (b), and (d)), 313–353K (c); and time 2 h ((a), (b), and (c)), 0–6 h ((d)).

reaction temperature exhibited a significant influence on the catalytic performance. With an increase in the reaction temperature, cyclohexene conversion gradually increased with decreased selectivity toward 1,2-diol (Fig. 6(c)). This may be due to the occurrence of the side reactions (e.g., self-condensation) of 1,2-diol at the external surface of the TiSn-Beta catalyst at high reaction temperatures. The effect of the amount of H_2O_2 on the catalytic performance of the TiSn-Beta zeolites was also investigated, and the results are shown in Fig. S5. With an increase in the amount of H_2O_2 , cyclohexene conversion gradually increased with a simultaneous decrease in the selectivity toward diols. Considering the requirements of high yield and high selectivity for diols, the initial substrate/ H_2O_2 ratio was set to 1.

Under identical reaction conditions, that is, at a reaction temperature of 333 K and with acetone as the solvent, the kinetic plots of cyclohexene conversion exhibited enhanced cyclohexene conversion within the short time-on-stream of 3 h; thereafter, a stable cyclohexene conversion of $\sim 80\%$ was observed (Fig. 6(d)). Simultaneously, a slight decrease in 1,2-diol selectivity was observed, which might be because the Ti and/or Sn active sites were covered by bulky by-products, which can be verified by recycling experiments. After the reaction, the catalyst was separated from the reaction mixture by centrifugation, washed with acetone, and dried at 353 K overnight. The recycled catalyst was used for the next cycle under the same reaction conditions. A sharp decrease in cyclohexene conversion from 74.6% to 50.1% occurred after four reaction cycles (Fig. 7(a)). This decrease clearly indicates that the bulky by-products cannot be completely removed by simple washing. However, when the spent TiSn-Beta catalyst was regenerated by calcination at 873 K in flowing air, the complete recovery of the catalytic activity with almost no changes in cyclohexene conversion and 1,2-diol selectivity was achieved after four cycles (Fig. 7(b)). In addition, the possibility of Ti and Sn leaching as well as structural and textural property changes of the zeolite catalyst during the reaction and regeneration could be excluded according to the ICP, BET, XRD, and UV-vis results (Ta-



Fig. 7. Recycling tests of cyclohexene conversion catalyzed by TiSn-Beta zeolite without (a) and with calcination (b). Reaction conditions: 5 mmol cyclohexene, 2.5 mL of MeCOMe, 5 mmol H₂O₂, 0.1 g of catalyst, temperature 333 K, and time 2 h. XRD patterns (c) and UV-vis spectra (d) of the fresh and spent TiSn-Beta catalyst after 4 cycles.

ble 1, Figs. 7(c,d)).

Bifunctional TiSn-Beta zeolite was observed to be an efficient solid Lewis acid catalyst for the direct conversion of cyclohexene to 1,2-cyclohexanediol. The excellent catalytic performance, originating from the bifunctional Lewis acid Ti and Sn sites confined in zeolite cages, as well as the desirable recyclability demonstrate the potential of this material for the tandem conversion of alkenes to 1,2-diols. As expected, high conversion can be achieved for most cyclic alkene substrates, while the selectivity for 1,2-diols differs significantly (Table 2). For unsaturated ketones, the C=O groups can adsorb on the strong Lewis acidic Sn sites and make them inaccessible for further epoxide hydration; thus, high selectivity for epoxide could be achieved. Furthermore, a decrease in the conversion of the substrates with substituted methyl groups was observed, implying that steric constraints on the substrate should be considered.

4. Conclusions

In summary, a tandem Lewis acid catalysis procedure within zeolite cages was successfully developed as a novel approach for the one-pot conversion of alkenes to 1,2-diols. While hydrogen peroxide solution can function as the oxidant (H_2O_2) for alkene epoxidation and nucleophile (H_2O) for epoxide hydration, the isolated Lewis acid Ti and Sn sites in the TiSn-Beta zeolite can efficiently integrate alkene epoxidation and epoxide hydration in tandem in one reactor. The zeolite confinement

Table 2

-

Catalytic performance of TiSn-Beta for the conversion of various alkenes.

C 1	Conversion	Selectivity (%)			
Substrate	(%)	Epoxide	1,2-Diol	Others	
\bigcirc	74.6	0.4	93.4	6.2	
\bigcirc	57.5	1.2	78.6	20.2	
\bigcirc	79.8	3.7	70.2	26.1	
	46.1	95.8	4.2	0	
O O	71.4	91.5	7.4	1.1	
	6.7	32.6	22.1	45.3	

Reaction conditions: 5 mmol substrate, 2.5 mL of MeCOMe, 5 mmol $\rm H_2O_2, 0.1$ g of catalyst, 333 K, and 2 h.

effect provides high tandem rates of alkene epoxidation and subsequent epoxide hydration as well as high selectivity for the desired product. Under identical conditions, a high yield of ~70% with >90% selectivity for 1,2-diols could be achieved over the bifunctional Lewis acidic TiSn-Beta zeolite. This study not only shows that zeolites are the ideal support materials for developing isolated multifunctional sites with desirable stability and catalytic activity but also shows the potential of these catalysts for applications in tandem catalytic reactions.

Electronic supporting information

Supporting information is available in the online version of this article.

References

- A. Seidel, Kirk-Othmer Encyclopedia of Chemical Technology, Wiley: New York, 2005.
- [2] L. M. Reed, L. A. Wenzel, J. B. O'Hara, Ind. Eng. Chem., 1956, 48, 205–208.
- [3] V. F. Shvets, R. A. Kozlovskiy, I. A. Kozlovskiy, M. G. Makarov, J. P. Suchkov, A. V. Koustov, Org. Process Res. Dev., 2005, 9, 768–773.
- [4] Y. Li, S. Yan, B. Yue, W. Yang, Z. Xie, Q. Chen, H. He, *Appl. Catal. A*, 2004, 272, 305–310.
- [5] Y. Li, S. Yan, L. Qian, W. Yang, Z. Xie, Q. Chen, B. Yue, H. He, J. Catal., 2006, 241, 173–179.
- [6] J. W. Van Hal, J. S. Ledford, X. Zhang, Catal. Today, 2007, 123, 310–315.
- [7] W. Li, L. Sun, L. Xie, X. Deng, N. Guan, L. Li, *Chin. J. Catal.*, **2019**, 40, 1255–1281.
- [8] B. Li, S. Bai, X. Wang, M. Zhong, Q. Yang, C. Li, Angew. Chem. Int. Ed., 2012, 51, 11517–11521.
- [9] W. Dai, C. Wang, B. Tang, G. Wu, N. Guan, Z. Xie, M. Hunger., L. Li, ACS Catal., 2016, 6, 2955–2964.
- [10] B. Tang, W. Dai, G. Wu, N. Guan, L. Li, M. Hunger, ACS Catal., 2014, 4, 2801–2810.
- [11] T. De Baerdemaeker, B. Steenackers, D. De Vos, Chem. Commun.,

2013, 49, 7474-7476.

- [12] B. Tang, W. Dai, X. Sun, N. Guan, L. Li, M. Hunger, Green Chem., 2014, 16, 2281–2291.
- [13] L. Chen, T. Xue, J. Ding, H. H. Wu, K. Zhang, P. Wu, M.-Y. He, *Chin. J. Catal.*, **2018**, 39, 275–282.
- [14] M. J. Climent, A. Corma, S. Iborra, M. J. Sabater, ACS Catal., 2014, 4, 870–891.
- [15] T. L. Lohr, T. J. Marks, *Nat. Chem.*, **2015**, 7, 477–482.
- [16] K. Cheng, B. Gu, X. Liu, J. Kang, Q. Zhang, Y. Wang, Angew. Chem. Int. Ed., 2016, 55, 4725–4728.
- [17] K. Cheng, W. Zhou, J. Kang, S. He, S. Shi, Q. Zhang, Y. Pan, W. Wen, Y. Wang, *Chem*, **2017**, 3, 334–347.
- [18] N. Duyckaerts, M. Bartsch, I.-T. Tro-tus, N. Pfänder, A. Lorke, F. Schüth, G. Prieto, *Angew. Chem. Int. Ed.*, **2017**, 56, 11480–11484.
- [19] Q. Sun, N. Wang, T. Zhang, R. Bai, A. Mayoral, P. Zhang, Q. Zhang, O. Terasaki, J. Yu, *Angew. Chem. Int. Ed.*, **2019**, 58, 18570–18576.
- [20] Z.-H., Zhou, X. Zhang, Y.-F. Huang, K.-H. Chen, L.-N. He, *Chin. J. Catal*, 2019, 40, 1345–1351.
- [21] B. B. Sarma, J. Kim, J. Amsler, G. Agostini, C. Weidenthaler, N. Pfänder, R. Arenal, P. Concep-ción, P. Plessow, F. Studt, G. Prieto, *Angew. Chem. Int. Ed.*, **2020**, 59, 5806–5815.
- [22] J. Kang, S. He, W. Zhou, Z. Shen, Y. Li, M. Chen, Q. Zhang, Y. Wang, *Nat. Commun.*, 2020, 11, 827–837.
- [23] H. J. Cho, D. Kim, J. Li, D. Su, B. Xu, J. Am. Chem. Soc., 2018, 140, 13514–13520.
- [24] H. J. Cho, D. Kim, S. Li, D. Su, D. Ma, B. Xu, ACS Catal., 2020, 10, 3340–3348.
- [25] T. Yan, S. Yao, W. Dai, G. Wu, N. Guan, L. Li, *Chin. J. Catal.*, **2021**, 42, 595–605.
- [26] T. Blasco, M. A. Camblor, A. Corma, P. Esteve, J. M. Guil, A. Martínez, J. A. Perdigón-Melón, S. Valencia, *J. Phys. Chem. B*, **1998**, 102, 75–88.
- [27] A. Corma, L. T. Nemeth, M. Renz, S. Valencia, *Nature*, 2001, 412, 423–425.
- [28] Y. Zhu, G. Chuah, S. Jaenicke, Chem. Commun., 2003, 2734–2735.
- [29] A. Corma, F. X. Llabrés i Xamena, C. Prestipino, M. Renz, S. Valencia, J. Phys. Chem. C, 2009, 113, 11306–11315.
- [30] H. Li, Q. Lei, X. Zhang, J. Suo, Catal. Commun. 2009, 10, 1936–1939.
- [31] X. Lu, H. Xu, J. Yan, W. Zhou, A. Liebens, P. Wu, J. Catal., 2018, 358,

Graphical Abstract

Chin. J. Catal., 2021, 42: 1176–1184 doi: 10.1016/S1872-2067(20)63734-2

Tandem Lewis acid catalysis for the conversion of alkenes to 1,2-diols in the confined space of bifunctional TiSn-Beta zeolite

Qifeng Lei, Chang Wang, Weili Dai *, Guangjun Wu, Naijia Guan, Michael Hunger, Landong Li

Nankai University, China; University of Stuttgart, Germany

Bifunctional TiSn-Beta zeolite was fabricated using a simple and scalable post-synthesis approach, and it was employed as an efficient catalyst for the tandem conversion of alkenes to 1,2-diols. The isolated Lewis acid Ti and Sn sites within the TiSn-Beta zeolite could efficiently integrate alkene epoxidation and epoxide hydration in tandem to achieve the selective conversion of alkenes into 1,2-diols with a high selectivity of >90%.



1184

89–99.

- [32] D. Yu, W. Dai, G. Wu, N. Guan, L. Li, Chin. J. Catal., 2019, 40, 1375–1384.
- [33] W A. C. Alba-Rubio, J. L. G. Fierro, L. León-Reina, R. Mariscal, J. A. Dumesic, M. López Granados, *Appl. Catal., B*, **2017**, 202, 269–280.
- [34] N. Jappar, Q. Xia, T. Tatsumi, J. Catal., 1998, 180, 132–141.
- [35] K. A. Koyano, T. Tatsumi, *Chem. Commun.*, **1996**, 145–146.
- [36] P. Li, G. Liu, H. Wu, Y. Liu, J.-g. Jiang, P. Wu, J. Phys. Chem. C, 2011, 115, 3663–3670.
- [37] C. Hammond, S. Conrad, I. Hermans, Angew. Chem. Int. Ed., 2012, 51, 11736–11739.
- [38] R. Bermejo-Deval, R. S. Assary, E. Nikolla, M. Moliner, Y.

Román-Leshkov, S.-J. Hwang, A. Palsdottir, D. Silverman, R. F. Lobo, L. A. Curtiss, M. E. Davis, *Proc. Natl. Acad. Sci. USA*, **2012**, 109, 9727–9732.

- [39] W. R. Gunther, V. K. Michaelis, M. A. Caporini, R. G. Griffin, Y. Román-Leshkov, J. Am. Chem. Soc., 2014, 136, 6219–6222.
- [40] S. Lang, M. Benz, U. Obenaus, R. Himmelmann, M. Hunger, *Chem-CatChem*, 2016, 8, 2031–2036.
- [41] T. Yan, W. Dai, G. Wu, S. Lang, M. Hunger, N. Guan, L. Li, ACS Catal., 2018, 8, 2760–2773.
- [42] T. Yan, L. Yang, W. Dai, G. Wu, N. Guan, M. Hunger, L. Li, ACS Catal., 2019, 9, 9726–9738.
- [43] H. Wu, B. Zhang, H. Liang, L. Zhai, G. Wang, Y. Qin, *The Innovation*, 2020, 1, 100029.

双功能TiSn-Beta分子筛限域的串联Lewis酸催化烯烃生成1,2-二醇

雷琦锋^a, 王 畅^a, 戴卫理^{a,*}, 武光军^a, 关乃佳^{a,b}, Michael Hunger^c, 李兰冬^{a,b} ^a南开大学材料科学与工程学院, 国家新材料研究院, 天津300350, 中国 ^b南开大学先进能源材料化学教育部重点实验室, 化学化工协同创新中心, 天津300071, 中国 ^c斯图加特大学化学技术研究所, 斯图加特70550, 德国

摘要: 1,2-二醇主要由环氧化合物水合产生、广泛用于防冻剂,聚酯树脂和医药等化学品中间体的生产.研究表明,具有 Lewis酸性的含锡沸石分子筛在环氧化物的水合反应中表现出优异的催化性能.环氧化合物是众所周知的碳亲电体之一, 主要由烯烃环氧化生成.含Ti(IV)沸石,如Ti-Beta和TS-1,是烯烃环氧化反应的高效催化剂.串联催化可以将多步反应整合 为一次反应,无需分离中间体,有效缩短合成路线,提高生产效率.因此,双功能Ti和Sn分子筛有望应用于烯烃制二醇的串 联催化反应中,即烯烃在Ti活性位点上发生环氧化反应,随后在Sn位点上发生水合反应,进而串联一步生成1,2-二醇.在沸 石分子筛中产生孤立的多功能活性位点是将多步反应整合成串联催化反应的一种有吸引力的设计策略.

本文通过简单且可规模制备的后合成路线构建了双功能TiSn-Beta分子筛,并用于烯烃串联催化制1,2-二醇反应.一方面,该反应中的过氧化氢溶液既能提供氧化剂(如H₂O₂)用于烯烃环氧化反应,又能提供环氧化合物水合反应的亲核试剂(如H₂O);同时TiSn-Beta作为一种高效双功能催化剂,孤立的Ti和Sn活性中心可以有效地将烯烃环氧化反应和环氧化物水合反应串联在沸石微反应器中,实现烯烃一步转化为1,2-二醇.另一方面,沸石的限域效应较好地保证了烯烃环氧化和环氧化物水合的高串联速率和目标产物的高选择性,在最优的反应条件下,1,2-二醇选择性高达90%以上,收率接近70%.本文结果表明沸石分子筛是构筑多功能孤立活性位点的理想载体,为其他串联反应催化剂的设计提供了良好的借鉴. 关键词:串联催化剂;限域效应;分子筛;烯烃环氧化;环氧化合物水合

收稿日期: 2020-09-22. 接受日期: 2020-11-02. 上网时间: 2021-03-05.

*通讯联系人. 电话/传真: (022)85358536; 电子信箱: weilidai@nankai.edu.cn

基金来源: 天津市自然科学基金(18JCJQJC47400, 18JCZDJC37400); 中央高校基本科研业务经费.

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(http://www.sciencedirect.com/journal/chinese-journal-of-catalysis).