MWW-Type Titanosilicate Synthesized by Simply Treating ERB-P Zeolite with Acidic H$_2$TiF$_6$ and Its Catalytic Performance in a Liquid Epoxidation of 1-Hexene with H$_2$O$_2$

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ABSTRACT: Synthesis of a Ti-incorporated zeolite using a simple and economical method has recently become a focus of attention. The direct hydrothermal synthesis of Ti-MWW is most commonly applied; however, it is challenging to perform and exhibits low titanium utilization. An innovative strategy of synthesizing Ti-MWW is proposed in the present study by simply treating the ERB-1 precursor of an MWW-type boron silicate with a H$_2$TiF$_6$/HNO$_3$ solution. This significantly shortens the Ti grafting process from 5 days to only a few hours and reduces the use of the structure-directing agent hexamethyleneimine (HMI); furthermore, no extraframework Ti is observed in the precursor, indicating good atomic economy. Typically, a piperidine (PI)-treated sample Ti-MWW$_{2-1}$-PI exhibits a higher conversion (76.6%) than the original Ti-MWW (44.8%) in the epoxidation of 1-hexene. X-ray diffraction (XRD), inductively coupled plasma (ICP), and transmission electron microscopy (TEM) techniques are used to explain in detail the probable mechanism underlying the incorporation of Ti species into the MWW framework. X-ray photoelectron spectroscopy (XPS) is employed to study the coordinate state of the Ti and F species in the samples after treatment with a piperidine solution. This method can be applied to synthesize other kinds of lamellar-structured zeolites with heteroatoms.

1. INTRODUCTION

Titanosilicates have been widely applied in the production of various oxygenates with the use of H$_2$O$_2$ as an environmentally friendly oxidant in olefin liquid epoxidation,$^{1,2}$ ammoximation,$^{3,4}$ and phenol hydroxylation$^{5,6}$ processes. Highly efficient selective oxidation is associated with a uniform pore structure, hydrophobicity,$^{7,8}$ and, most importantly, unique tetracoordinated titanium species.$^{9-11}$ The hydrothermal method is commonly applied to synthesize zeolites with tetracoordinated titanium species, but this method requires a larger amount of organic structure-directing agent (OSDA)$^{12}$ than pure silicate.$^{13}$

To simplify the synthesis process, a new approach to introduce Ti active sites into the framework has been established: grafting titanium in highly dealuminized silicates.$^{14-18}$ With either a solid–gas treatment, with, for example, TiCl$_4$ or a solid–liquid modification, with, for example, a Ti(acac)$_3$,O$i$P$_2$, isopropanol solution, it is not difficult to synthesize a Ti-incorporated zeolite and conserve the use of OSDA. Hence, the presence of extraframework octahedral-coordinated titanium species severely hinders the catalytic performance of epoxidation with hydrogen peroxide.$^{16,19}$ These zeolite types are preferred to catalyze bulk molecules with tert-butyl hydroperoxide (TBHP). Therefore, a catalyst that exhibits only tetracoordinated titanium species by hydrothermal synthesis is highly desirable.

Wu et al.$^{20-22}$ promoted a postsynthesis method to obtain a simultaneous isomorphic substitution. This innovative method was applied in a zeolite with unique properties, in which the structure could reversibly change between a two-dimensional (2D) and three-dimensional (3D) topology. Highly deboronated ERB-1 was stirred with a piperidine (PI) water solution containing Ti species at the crystallization temperature. At this temperature, piperidine/tetrabutyl orthotitanate (TBOT) was present in the interlayer region and could facilitate the immigration of Ti species into the framework.$^{23,24}$ Organic Ti species were later hydrolyzed to form silica hydroxyl nests during a deboronation process. The Ti-MWW precursor was further acid-washed to eliminate extraframework Ti species and then calcined at 823 K for 6 h. Therefore, we expect that the synthesis of Ti-MWW will not be
difficult if we can complete the simultaneous acidic deboronation and titanium hydrolysis of an MWW 2D-layered structure.

According to a previous study, organic Ti, such as TBOT, plays an important role as a Ti source in the synthesis of titanosilicate. Thus, it is difficult to control its hydrolysis rate, especially under acidic conditions. Therefore, the proposed method has extensive application prospects for synthesizing zeolite from inorganic reactants. The proposed method refers to the previous postsynthesis approach wherein inorganic titanium materials (NH₄)₂TiF₆ and H₂TiF₆ are employed as a Ti source and the structure of a boron-containing MWW framework is reversed to a Ti-MWW-type catalyst. The mechanism can also be described as follows: silica hydroxyl nests are formed by eliminating silica atoms in the framework, while simultaneously, inorganic Ti hydrolysis occurs in the structure. The above method selectively produces tetracoordinated titanium species. TS-1, which was prepared with TPABr, colloidal silica, and Ti(SO₄)₂ in a hydrothermal synthesis process, performed well in epichlorohydrin epoxidation; however, the as-synthesized samples needed to be acid-washed to eliminate extraframework Ti species before they could exhibit high catalytic performance.

In this work, a B-containing MWW-type precursor ERB-p was prepared by a dry-gel conversion (DGC) method. A series of Ti-MWW zeolites could be obtained by treating the ERB precursor with a certain amount of H₂TiF₆/HNO₃ solution, made with different concentrations of HNO₃ solution and with various reaction times. Ti-MWW could be obtained by direct calcination because the as-synthesized samples exhibited no extraframework titanium species.

2. RESULTS AND DISCUSSION

2.1. Influence of Ti Content on Epoxidation of 1-Hexene. To optimize the Si/Ti ratio, ERB-p was washed with different concentrations of H₂TiF₆ in a 2 M HNO₃ solution for 1 h at 378 K. Ti-MWW, with a Si/Ti ratio in the range of 10–160, was prepared.

Figure 1 shows the results of Ti-MWW synthesized with different Ti contents in the epoxidation of 1-hexene. The 1-hexene conversion first increased but then decreased with increasing Ti content. Interestingly, the selectivity of epoxide was found to increase dramatically from 54.7 to 84.0% when the Si/Ti ratio slightly changed from 40 to 20, which could be attributed to the interlayer expansion that was observed in the zeolite; the above result can be confirmed in Figure 2 with the appearance of the 002 diffraction peak.

Figure 2. XRD pattern of Ti-MWW with different Si/Ti ratios: (a) 40, (b) 20, and (c) 10.

The structure—activity relationship will be discussed later. Nevertheless, the yield of epoxide exhibited volcano-type behavior with the change in the Ti content and reached a maximum at a ratio of 20. Thus, Ti-MWW with a Ti content ratio of 20 was further investigated to reveal the mechanism for the introduction of H₂TiF₆ into the framework.

2.2. Mechanism of Introducing H₂TiF₆ into the Framework in Different Treatments. A postsynthesis approach was investigated by replacing boron in the boron-containing zeolite with Ti. However, the procedure needs to be separated into two steps: an acid treatment step and an additional step for the conversion of the 3D crystalline structure, which are caused by the direct calcination, into a 2D lamellar structure. Thus, the above procedure requires an extensive investigation to convert these two complicated steps to a procedure with only one step. An unstable interlayer structure provided a new approach to synthesize Ti-MWW from ERB-p, which required replacing a piperidine molecule in the interlayer region of ERB-p with a TiF₆⁻ ion. A cation acid treatment of zeolite was essential in this work because the OSDA molecules between the layers and causes interlayer condensation, which converts the original structure to a 3D crystalline structure and results in the disappearance of the 001 and [002] diffraction peaks. Moreover, the intensity of
the [002] peak increases with increasing HNO$_3$ concentration and duration of acid treatment. The relationship between the number of active sites (Ti) and the structure of the zeolite was investigated by the XRD patterns and ICP data. Figure 5 shows that a high Ti content is related to the increasing expansion of the interlayer structure (increasing intensity of the crystal surface I$_{002}$). The structure belonging to the 002 surfaces benefited the introduction of Ti species into the MWW structure. The XRD patterns shifted to a lower degree, which also indicated that Ti atoms were planted in the framework. However, the acidic H$_2$TiF$_6$ treatment was accompanied by an unexpectedly strong desilication process, as shown in Figure 3. ERB-1 had an average particle size of 3.5 μm, and the large secondary crystals, which were measured to be 1 μm, collided into the primary platelet crystals during the series of acid treatments. As shown in Figure 4D and 3g, the crystallinity of the MWW structure can be destroyed by acid treatment conditions that are too severe.

Ultraviolet–visible (UV–vis) spectra were obtained to analyze the coordinate state of Ti-MWW synthesized under different conditions. The band at approximately 220 nm was assigned to the ligand-to-metal charge transfer originating from the oxide ligand to Ti$^{4+}$ in a tetrahedral (Td) coordination. Figure 6 shows that no extraframework Ti species emerge during the acidic grafting, which is different from the as-synthesized Ti-MWW. This phenomenon indicated that the titanium atom was selectively inserted into the framework and produced Ti-MWW in a new atom-economical method. It also showed that the existence of an interlayer structure and proper acid treatment conditions dominated the grafting process as Ti-MWW$_{0-1}$, without HNO$_3$ assistance, and ERB-1$_{2-1}$ (using ERB-1 instead ERB-p), with no obvious [002] peak, appeared as extraframework Ti (band at approximately 260 nm) in the anatase phase (band at approximately 330 nm). As shown in Figure 7, Ti was not completely introduced into the framework because of the absence of piperidine in the interlayer and the assistance of HNO$_3$.

In addition, Ti-MWW prepared by treating ERB-p with acidic H$_2$TiF$_6$ exhibited an IR band at 945 cm$^{-1}$ (Figure 8), while the characteristic IR band at 960 cm$^{-1}$ was assigned to the stretching of Si–O–Ti bonds in the [Ti(OSiO$_3$)$_4$] unit. This result indicated that the Si–O–Ti bonds might be influenced by fluorine in the framework. The mechanism of Ti grafting could be concluded as follows: the desilication and deboronation (Si/B > 1000) process provided hydroxyl nests. During this procedure, acidic H$_2$TiF$_6$ partly replaced the piperidine and prevented the silanol in the interlayer from forming a condensation interlayer-expanded structure, and inorganic Ti hydrolysis on the hydroxyl nest selectively produced framework Ti, at the same time. The proposed mechanism for the incorporation of Ti species is shown in Figure 9.

The epoxidation of 1-hexene with H$_2$O$_2$ was selected as the probe reaction in this study. The samples could not show high performance without proper acid treatment conditions. Ti-MWW$_{0-1}$ achieved only 8.2% conversion and 43.6% selectivity, which could be attributed to the extraframework Ti. Ti-MWW synthesized by 1 M HNO$_3$ showed 39.2% conversion and 90.7% epoxide selectivity. The conversion increased sharply with an increasing concentration of HNO$_3$ (2 M) but demonstrated a low selectivity (84.0%) due to the inevitable
simultaneous insertion of Ti and F atoms. The decrease in epoxide yield with the extension of the acid treatment time also indicated that overused F atoms in the framework and zeolite structure caused a collapse in the structure due to its application in epoxidation reactions. For instance, no catalytic activity was observed with acid-treated ERB-1 because the structure transformed from a 2D lamellar structure to a 3D MWW structure after calcination, which inhibited Ti insertion.

2.3. Influence of PI Treatment on the Ti Coordinate State of Ti-MWW.

To overcome the negative impact of F\(^-\) in the framework and further improve the catalytic performance of Ti-MWW in the epoxidation of 1-hexene, a piperidine treatment was used. The amount of piperidine required was calculated by the amount of Ti species; for instance, one Ti ligand required one PI molecule. The state of the Ti and F species was analyzed by X-ray photoelectron spectroscopy.

Table 1. Chemical Composition of Ti-MWW Samples and the Results of Epoxidation of 1-Hexene with H\(_2\)O\(_2\)

| sample name     | product (Si/Ti ratio)\(^a\) | 1-hexene conversion (%) | TON\(^b\) (mol (mol\(^{-1}\)Ti)) | epoxide selectivity (%) | H\(_2\)O\(_2\)\(^c\) selectivity (%) |
|-----------------|-----------------------------|-------------------------|-----------------------------------|-------------------------|-----------------------------------|
| Ti-MWW\(_0\)-1  | 26                          | 8.2                     | 13                                | 43.6                    | 46.7                              |
| Ti-MWW\(_1\)-1  | 65                          | 39.2                    | 147                               | 90.7                    | 90.3                              |
| Ti-MWW\(_2\)-1  | 62                          | 56.6                    | 201                               | 84.0                    | 88.2                              |
| Ti-MWW\(_2\)-2  | 46                          | 53.5                    | 142                               | 82.5                    | 87.8                              |
| Ti-MWW\(_2\)-4  | 34                          | 49.2                    | 99                                | 76.2                    | 87.5                              |
| Ti-MWW\(_2\)-7  | 69                          | 41.0                    | 163                               | 86.9                    | 84.6                              |
| Ti-MWW\(_d\)-4  | 54                          | 44.8                    | 214                               | 99.0                    | 93.0                              |

\(^a\)Given by ICP. \(^b\)TON in mol (mol Ti)\(^{-1}\). \(^c\)Efficiency of H\(_2\)O\(_2\) = (amount of product/amount of H\(_2\)O\(_2\) consumed) \times 100\%. \(^d\)Data of Ti-MWW were from ref 17.

Figure 5. Ratio of the [002] peak and [100] peak intensity and the corresponding Si/Ti ratios in the series of catalysts: (A) Ti-MWW\(_0\)-1, (B) Ti-MWW\(_2\)-0.25, (C) Ti-MWW\(_2\)-1, (D) Ti-MWW\(_2\)-2, and (E) Ti-MWW\(_2\)-4.

Figure 6. UV–vis spectra of (a) Ti-MWW\(_2\)-1, (b) as-synthesized Ti-MWW\(_2\)-1, and (c) as-synthesized Ti-MWW.

Figure 7. UV–vis spectra of (a) Ti-MWW\(_2\)-1, (b) as-synthesized Ti-MWW\(_0\)-1, and (c) ERB\(_2\)-1 (using ERB-1 instead of ERB-p).

Figure 8. Fourier transform infrared (FT–IR) spectra of Ti-MWW and Ti-MWW\(_2\)-1.
(XPS), a surface-sensitive technique for the analysis of elements and their oxidation states. The results are shown in Figures 10 and 11. The binding energy of Ti 2p changed from 460.2 to 459.2 and 458.1 eV after the PI treatment, indicating that the Ti species in the tetrahedrally coordinated state may transform into two different forms.31 The low binding energy indicated the negative charge distribution of Ti atoms in Ti-MWW−1−PI. An F−-modified hydrothermal synthesis of Ti-MWW−32 exhibited SiF6−, SiO4/2F− units, and SiO3/2F units. The SiO3/2F units were considered beneficial to the epoxidation of 1-hexene in the literature; the above observation is due to the high electronegativity of the SiO3/2F unit withdrawing the electron around the Ti nucleus, thus reinforcing the activity of Ti4+. Hence, Ti-MWW synthesized by a direct acidic H2TiF6 treatment with ERB-p only had SiO4/2F− and SiF6− units in the framework, which was considered undesirable for the epoxidation reaction. After the piperidine treatment, the binding energy of F1s split into two peaks: 685 eV (F− in the SiF6− and SiO4/2F− units) and 688 eV (F in the SiO3/2F units). Furthermore, the F− units significantly transitioned to SiO3/2F−.

The catalytic performance was greatly enhanced by a simple piperidine treatment. The conversion of 1-hexene increased up to 76.6% when Ti-MWW−1 was used as the catalyst. The selectivity of epoxide and H2O2 also increased to 94.3 and 94.4%, respectively. The activity of the Ti-MWW−1 sample improved and was even higher than that of Ti-MWW−2−1 after the PI treatment; however, the selectivity of epoxide became even worse due to its poor crystallinity. We speculated that piperidine arranged F− into the framework and formed a more stable SiO3/2F− structure and that the ligands with open-site six-coordinate Ti species promoted the activation of H2O2 over Ti-MWW; thus, the above arrangement significantly enhanced the catalytic performance of the epoxidation of 1-hexene (Table 2).

As shown in Table 3, the catalytic activity of Ti-MWW−1−PI was higher than that of other typical titanium silicates, such as nanosized TS-1 and Ti-β, as well as other synthesized Ti-incorporated MWW-type zeolites. TS-1 in ref 34 is also an anatase-free type zeolite, which is fair for comparison with Ti-MWW synthesized in this work. TS-1 exhibited several advantages, including high epoxide and H2O2 selectivity and only a slight difference in the 1-hexene epoxidation conversion compared with Ti-MWW−2−1. The above results indicate that the TS-1 catalyst could also be a suitable candidate for linear olefin epoxidation in the absence of anatase in the framework. Ti-D-ERB-1-L-5h had a higher Ti content but lower 1-hexene conversion than Ti-MWW−1−PI. The higher catalytic performance in this work was attributed to the MWW topology and the absence of anatase and extraframework Ti.

3. CONCLUSIONS

In this study, an innovative strategy was discovered: Ti-MWW could be successfully synthesized by replacing the piperidine molecule in the interlayer region of ERB-p with a TiF62− ion. This method was much more efficient than a hydrothermal synthesis. The acidic H2TiF6 treatment conditions could be
neither too mild nor too severe. Ti-MWW2−1−y was optimized as a desired catalyst, showing higher catalytic performance than Ti-MWW in the epoxidation of 1-hexene with H2O2. Furthermore, the conversion of 1-hexene increased from 56.6% to 76.6% when the catalyst was treated with PI. Most importantly, if the 2D lamellar structure is treated with acidic H2TiF6, which is associated with the zeolite framework properties, then the proposed method might be applied to different zeolite types.

4. EXPERIMENTAL SECTION

4.1. Preparation of Ti-MWW. 4.1.1. Synthesis of ERB-1 Precursor. The ERB-1 precursor was synthesized by the DGC method. 28 Hexamethylenimine (HMI), boric acid, and ERB-1 36 were employed as the structure-directing agent (SDA), crystallization-supporting agent, and seed, respectively. In the DGC method, 2.0 g of SiO2 (A200, Degussa), 0.257 g of boric acid (SCRC), and 0.2 g of ERB-1 as the seed were mixed together and dissolved in 10 mL of deionized water to form a homogeneous gel. The resultant homogeneous gel was placed in a 373 K oil bath under stirring until the water was completely evaporated to get the silica-boric compound. The silica-boric compound was then transferred into a Teflon-lined autoclave containing 2 g of HMI and 4 g of deionized water. Crystallization was conducted in this autoclave at 443 K for 2 days. The solid product was washed with deionized water and dried at 383 K overnight, which was denoted as ERB-p.

4.1.2. ERB-p Treated with H2TiF6/HNO3. The ERB precursor consists of SiO2, HMI, and water, to synthesize Ti-MWW with a certain Si/Ti ratio. The amount of pure SiO2 was determined by thermogravimetry. In a typical synthesis procedure, 1.37 g of ERB-p (1 g pure SiO2) was mixed with 0.273 g of H2TiF6 (50% in aqueous, Aladdin) in 20 mL of X mole HNO3 solution. The mixture where the Si/Ti mole ratio equaled 20 was then placed in a 25 mL flask at 378 K for 1 h with a condenser. The as-synthesized Ti-MWW was obtained by washing and drying at 383 K overnight, and further calcined at 823 K for 6 h. The product prepared by ERB-p was denoted as Ti-MWWx−y. The piperdine modification experiment was conducted by treating 0.1 g of Ti-MWWx−y with 10 mL of a 10 mmol PL−water solution at 378 K with a condenser for 1 h, and Ti-MWWx−y−PL was obtained by additional filtration and drying.

4.2. Catalyst Characterization. X-ray diffraction (XRD) patterns were obtained using a Rigaku MiniFlex 600 X-ray diffractrometer with Cu Kα radiation at 45 kV and 20 mA over a 2θ range of 5–45°. The UV–vis diffuse reflectance spectra were recorded on a Lambda 950 spectrophotometer using BaSO4 as the reference. The micromorphology of the samples was characterized by a Hitachi S-8010 scanning electron microscope. X-ray photoelectron spectroscopy (XPS) patterns were carried out using an ESCALAB 250Xi (Thermo Scientific) instrument. The Ti content was measured by inductively coupled plasma optical emission (ICP) spectrophotometry (PerkinElmer OPTIMA 8000). FT-IR spectra were recorded by a Nicolet 6700 FT–IR spectrometer using the KBr technique, and the wafer was prepared with the same amount of sample and KBr under the same pressure.

4.3. Epoxidation of 1-Hexene. The liquid-phase oxidation of 1-hexene with hydrogen peroxide was carried out in a 25 mL flask with a condenser. In a typical run, 50 mg of catalyst, 10 mmol of H2O2 (30% aqueous solution, SCRC), 10 mmol of 1-hexene (Aladdin), and 10 mL of acetonitrile (99%, SCRC) were mixed in a reactor. The reaction was carried out at 333 K for 2 h under magnetic stirring. The catalyst was filtered, and the final reaction mixture was analyzed by a gas chromatograph (Agilent 6890) and quantified using cyclohexanone as an internal standard. The residual H2O2 was determined by a standard titration method with 0.1 M sodium thiosulfate.

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Notes

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