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Synthesis of Expanded Titanosilicate MWW-Related Materials from a Pure Silica Precursor[†]

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ABSTRACT: Titanosilicate forms of expanded MWW-related material are synthesized starting from a pure silica precursor, ITQ-1. This procedure improves the current synthetic route of the expanded titanosilicate MWW material (Ti-YNU-1), which requires the use of a borosilicate MWW as precursor and, consequently, several postsynthetic acid treatments for removing boron atoms from the framework. The expanded Ti-MWW-related materials presented here show better activity than regular Ti-MWW in the selective epoxidation reaction of cyclohexene using H_2O_2 as oxidant.



KEYWORDS: titanosilicate, MWW, zeolite, olefin epoxidation, green chemistry

1. INTRODUCTION

In the last decades, the introduction of isolated metals, especially titanium, in the walls of porous silicates has promoted those materials as very efficient catalysts for the selective oxidation of hydrocarbons using peroxides as oxidants.¹ Since the discovery of medium-pore titanosilicate TS-1 in 1983,² other molecular sieves containing isolated Ti atoms in tetrahedral coordination have been synthesized with diverse pore architectures. Specific structures would induce the adequate activity and selectivity toward oxygenated derivates, depending on the size of reactants.³ In this sense, large-pore titanosilicates are required to facilitate the reactant accessibility to the active sites when bulky organic molecules are tested. Significant large-pore titanosilicates have been described in the literature, such as Ti-Beta,⁴ Ti-ZSM-12,⁵ Ti-MOR,⁶ Ti-ITQ-7,⁷ or Ti-BEC.⁸

A very fascinating structure is the case of the MWW material, which is formed by two independent noninterconnected pore systems both having 10-membered ring (MR) openings.⁹ One of these systems is defined by a two-dimensional sinusoidal channel, and the other comprises supercages of $7.1 \times 7.1 \times 18.2$ Å.¹⁰ MWW is typically obtained from the calcination of an MWW-lamellar precursor, and interestingly, this lamellar can also be expanded into microporous–mesoporous hybrids¹¹ or delaminated into nanosheets.¹²

The preparation of the titanosilicate form of MWW was first described by Tatsumi et al.¹³ by combining the hydrothermal synthesis of the titanoborosilicate MWW, followed by acid treatments to selectively remove boron atoms. Because the direct preparation of MWW-type titanosilicate from gels containing only Si and Ti in the absence of alkali cations is difficult,¹⁴ the above-described methodology is very effective in

achieving the Ti-MWW material. In this case, boron is used as a structure-supporting agent in the direct preparation of the titanoborosilicate MWW, and afterward, the sample is deboronated by posterior acid treatments.¹⁵ It is claimed that this Ti-MWW material shows higher catalytic activity than other relevant titanosilicates, such as TS-1 and Ti-Beta, in the liquid-phase epoxidation of linear alkenes with H_2O_2 .¹⁶

However, bulkier alkenes, such as cyclohexene, suffer severe restrictions when diffusing through the medium pores of the MWW material, reducing considerably their activity in the liquid-phase epoxidation reaction.¹⁷ To avoid those steric restrictions, Tatsumi et al. have described the synthesis of the Ti-YNU-1 material,¹⁸ which is structurally related to MWW zeolite, but introducing titanium atoms as pillars in the interlayer region.¹⁹ Ti-YNU-1 allows the reactivity of bulky organic molecules due to the slight expansion of the pore diameter by the presence of Ti atoms in the interlayer region.

The Ti-YNU-1 material is synthesized following a rationalized methodology based on several steps, using as the initial precursor the borosilicate form of MWW.^{18,20} The MWW precursor is acid-treated several times to selectively remove boron atoms, and subsequently, the deboronated precursor is mixed with an organic molecule and a Ti source to afford the titanosilicate material.¹⁸ Nevertheless, the use of B-MWW as precursor introduces some drawbacks in the synthesis procedure. Most relevant, several acid treatments are required for removing most of the boron from the MWW materials, and if complete elimination of boron from the framework or from

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the pores is not achieved, its presence can negatively influence the activity and selectivity of the catalyst.²¹

Herein, we will synthesize expanded titanosilicate MWWrelated materials starting from a pure silica MWW precursor, avoiding the use of the structure-supporting agent (boron). This procedure will involve the use of the pure silica MWW zeolite in combination with the Ti source and one of the organic molecules required in the typical preparation of MWW materials. This methodology will improve the synthetic route previously reported, since the acid treatments required to selectively remove the structure-supporting agent (boron), with the associated inconvenience if it is not very well removed, will be avoided. The expanded Ti-MWW-related materials will be characterized in order to study their crystalline nature, the coordination of Ti species, and their pore size distribution. Finally, the expanded Ti-MWW-related materials will be tested on the selective epoxidation reaction of cyclohexene with H_2O_{22} and their catalytic activity compared to the regular Ti-MWW.

2. EXPERIMENTAL SECTION

2.1. Zeolite Synthesis. Synthesis of N,N,N-Trimethyl-1-adamantammonium. A 29.6 g portion of 1-adamantamine (Sigma-Aldrich) and 64 g of potassium carbonate (Sigma-Aldrich) were mixed with 320 mL of chloroform. At this point, 75 g of methyl iodide was added dropwise while the reaction was stirred in an ice bath. The reaction was maintained during 5 days under agitation at room temperature. The mixture was filtered and washed with diethyl ether, and the resultant solid was further extracted with chloroform. The final product was N,N,N-trimethyl-1-adamantammonium iodide. This iodide salt was anion-exchanged using an ion-exchange resin to prepare the corresponding hydroxide form.

Synthesis of Pure Silica MWW (ITQ-1). A 113.34 g portion of an aqueous solution of N_rN_r -trimethyl-1-adamantammonium hydroxide (7.5 wt %) was mixed with 26.9 g of water and 5.12 g of hexamethylenimine. A 0.97 g portion of sodium chloride and 10 g of silica (Aerosil 200, Degussa) were then added to the mixture, keeping the gel under stirring during 30 min. The gel was transferred to an autoclave with a Teflon liner and heated to a temperature of 150 °C during 9 days under agitation (60 rpm) conditions. The sample after hydrothermal crystallization was filtered and washed with abundant distilled water and finally dried at 100 °C.

Synthesis of Expanded Ti-MWW-Related Materials. a. Ti-MWWexp(1). A 289 mg portion of piperidine (99%, Sigma-Aldrich) was mixed with 294 mg of water and 34 mg of titanium(IV) butoxide (97%, Sigma-Aldrich). The mixture was stirred during 30 min until complete hydrolysis of titanium(IV) butoxide. The calcined pure silica ITQ-1 precursor (200 mg) synthesized above was then added to the mixture, keeping the gel under stirring during 30 min. The final gel composition was SiO₂:0.033 Ti:1.0 piperidine:5 H₂O. The gel was transferred to an autoclave with a Teflon liner and heated to a temperature of 175 °C during 7 days under static conditions. The sample after hydrothermal crystallization was filtered and washed with abundant distilled water and finally dried at 100 °C.

The as-synthesized titanosilicate MWW-related material was acidtreated using nitric acid (2 M) for 16 h at 100 $^{\circ}$ C (1 g of material in 20 mL of nitric acid solution) for removing octahedral Ti species. The resultant sample was calcined at 550 $^{\circ}$ C in air.

b. Ti-MWW-exp(2). A 608 mg portion of piperidine (99%, Sigma-Aldrich) was mixed with 618 mg of water and 16 mg of titanium(IV) butoxide (97%, Sigma-Aldrich). The mixture was stirred during 30 min until complete hydrolysis of titanium(IV) butoxide. The calcined pure silica ITQ-1 precursor (421 mg) synthesized above was then added to the mixture, keeping the gel under stirring during 30 min. The final gel composition was SiO₂:0.0067 Ti:1.0 piperidine:5 H₂O. The gel was transferred to an autoclave with a Teflon liner and heated to a temperature of 175 °C during 7 days under static conditions. The sample after hydrothermal crystallization was filtered and washed with abundant distilled water and finally dried at 100 °C.

The as-synthesized titanosilicate MWW-related material was acid treated using nitric acid (2 M) for 16 h at 100 $^\circ\mathrm{C}$ (1 g of material in 20 mL of nitric acid solution) for removing octahedral Ti species. The resultant sample was calcined at 550 $^\circ\mathrm{C}$ in air.

Synthesis of Regular Ti-MWW Material. Regular Ti-MWW was prepared following the methodology described by Tatsumi et al. in ref 16. Titanoborosilicate precursor was synthesized from a gel using piperidine as an organic structure-directing agent, a Si/B molar ratio of 0.75, and a Si/Ti molar ratio of 50. To properly remove boron atoms, the calcined sample was acid-treated by refluxing 6 M HNO₃ during 12 h. This acid treatment was repeated three times, until chemical analyses revealed a Si/B ratio higher than 500.

2.2. Characterization. Synthesized samples were characterized by powder X-ray diffraction using a multisample Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 45 kV and 40 mA, and using Cu K α radiation ($\lambda = 0.1542$ nm).

The chemical analysis was performed on a 715-ES ICP-Optical Emission spectrometer, after solid dissolution in HNO₃/HCl/HF aqueous solution. The organic content of the as-made materials was determined by elemental analysis performed on a SCHN FISONS elemental analyzer.

Pore size distribution was determined by Ar adsorption measured on a Micromeritics ASAP 2020 at 87 K.

UV–vis spectra were obtained with a Perkin-Elmer (Lambda 19) spectrometer equipped with an integrating sphere with ${\rm BaSO_4}$ as reference.

2.3. Catalytic Tests. Catalytic tests by using H_2O_2 as oxidant were performed at 333 K, using 50 mg of catalyst and the following reaction mixture: 10 mmol of cyclohexene, 10 mmol of H_2O_2 , and 10 mL of acetonitrile. All substances were available from Sigma-Aldrich Company (acetonitrile, 99%; cyclohexene, 99%; H_2O_2 , 35 wt % in water). Aliquots were analyzed by gas chromatography using nonane as the standard. H_2O_2 efficiency was calculated by iodometric tritation.

3. RESULTS AND DISCUSSION

To prepare the expanded titanosilicate form of the MWWrelated material, avoiding the use of structure-supporting



Figure 1. Powder X-ray diffraction (PXRD) patterns of the different MWW-related materials.

agents, such as boron, the pure silica MWW precursor must be synthesized. All-silica MWW, called ITQ-1, can be prepared using N,N,N-1-trimethyladamantammonium (TMAda), or a mixture of TMAda and hexamethylenimine (HMI) as organic structure-directing agents (OSDAs).²² As observed in the original patent, the combination of the small amine (HMI) and the quaternary ammonium cation (TMAda) not only allows

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Table 1. Chemical Analyses of the Different Titanosilicates

Si/Ti	Si/B
43	9.6
68	>500
41	
58	
146	
159	
	Si/Ti 43 68 41 58 146 159



Figure 2. UV-vis DRS spectra of different MWW-related materials.



Figure 3. Pore size distribution of Ti-MWW and expanded Ti-MWW-related materials obtained from argon adsorption.

reducing the required synthesis time²³ but also obtaining ITQ-1 with better crystallinity.²² Consequently, ITQ-1 was prepared by using the cooperative directing effects of both organic molecules (see synthesis details in the Experimental Section). The powder X-ray diffraction (PXRD) pattern obtained for this sample is the characteristic of the crystalline lamellar MWW precursor (see "ITQ-1" diffraction pattern in Figure 1). The asprepared pure silica ITQ-1 material was calcined at 550 °C during 6 h to remove the organic.

For the preparation of the titanosilicate MWW-related structure, the calcined all-silica ITQ-1 sample was used directly without further treatments. This is an important difference with the previous methodology where several acid treatments were required to selectively remove boron atoms from the used



Figure 4. SEM images of Ti-MWW (top) and Ti-MWW-exp(1) (bottom).



Figure 5. Catalytic results of Ti-MWW and Ti-MWW-exp(1) in the oxidation of cyclohexene with H_2O_2 .

borosilicate precursor. The siliceous precursor ITQ-1 was introduced in an aqueous synthesis media with an organic structure-directing agent, such as piperidine (PI), and a titanium precursor, such as titanium(IV) butoxide, obtaining a gel with the following molar composition: SiO₂:0.033 Ti:1.0 piperidine:5 H₂O. The gel was autoclaved at 175 °C during 7 days, and after that period, the resultant solid was recovered by filtration. This solid, called "Ti-ITQ-1(1)", mostly retains the MWW lamellar precursor nature (see 001 and 002 reflections in Figure 1). The incorporation of Ti in the final solid was measured by chemical analyses, and the results give a Si/Ti molar ratio of 41 (see Table 1). Ti-ITQ-1(1) was also studied by UV–vis spectroscopy to identify the coordination of Ti species. As observed in Figure 2, the Ti-ITQ-1(1) material

Table 2. Oxidation of C	yclohexene with H ₂ O	, in Acetonitrile over	Ti-MWW and Exp.	anded Ti-MWW-l	Related Materials"
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catalyst	Si/Ti	<i>t</i> (h)	X_{cycloh} (%)	TOF^b (mol conv/h·mol Ti)	$X_{{ m H}_2{ m O}_2}$ (%)	S_{Epox} (%)
Ti-MWW	68	5	5	28	68	93
Ti-MWW-exp(1)	58	5	35	100	73	95
Ti-MWW-exp(2)	159	5	18	243	69	94
					1	

^{*a*}Reaction conditions: 0.05 g of catalyst, 10 mmol of cyclohexene, 10 mmol of H_2O_2 , 10 mL of acetonitrile, 333 K. ^{*b*}Turnover frequency number calculated from initial reaction rates (mol of cyclohexene converted/h·mol Ti).

shows two clearly identified bands, one centered at 220 nm, and the other at 260 nm. The first band has been assigned to titanium species in tetrahedral coordination in zeolite framework positions, while the second band has been assigned to titanium species in octahedral coordination in extraframework positions.²⁴ Unfortunately, octahedral Ti species could direct the formation of the stable anatase phase after calcination procedures, whose presence affects negatively the selectivity for oxidation reactions.

It has been described that, by washing the as-prepared titanosilicates with acid under reflux before calcination, the Ti species in octahedral coordination can be removed, while the expanded nature of the layered MWW can be retained after calcination.^{17,18} Taking into account these two premises, an acid treatment with nitric acid was performed before the calcination of the Ti-ITQ-1(1) sample (see the Experimental Section for details). The resulting sample, named "Ti-MWWexp(1)", shows a unique band at 220 nm (see the UV-vis spectrum in Figure 2). Therefore, all octahedral Ti species have been selectively removed, achieving a Si/Ti molar ratio in the final solid of 58 (see Table 1). However, the PXRD pattern of the Ti-MWW-exp(1) material (see Figure 1) shows a very weak 001 reflection, indicating that most of the layered structure of the MWW precursor was not retained. Similar behavior has been previously observed by Tatsumi et al. when the Si/Ti ratio in the gel was decreased.¹⁷ They described that, when the Si/Ti ratio was lowered to 50, the appearance of the expanded layered structure was reduced after the acid treatment and calcination.

Consequently, we attempted the synthesis of the titanosilicate form of the MWW-related material with a higher Si/Ti ratio (150), in order to study the effect of the Ti content on the formation of the expanded layered structure following our synthesis methodology. Pure silica ITQ-1 was mixed in aqueous media with piperidine, and titanium(IV) butoxide, achieving the following gel composition: SiO₂:0.0067 Ti:1.0 piperidine:5 H₂O. After 7 days at 175 °C, the obtained solid shows the characteristic PXRD of the lamellar MWW precursor (see 001 and 002 reflections of Ti-ITQ-1(2) in Figure 1). As it can be seen in Figure 1, the PXRD patterns of Ti-ITQ(1) and Ti-ITQ-1(2) are very similar, but both samples contain very different Ti contents (Si/Ti ratios of 41 and 146, respectively; see Table 1). Very interestingly, after the acid treatment on the as-prepared Ti-ITQ(2) sample to selectively remove octahedral Ti species, and its posterior calcination, the resultant material, "Ti-MWWexp(2)", mostly preserves the layered structure (see 001 and 002 reflections of Ti-MWW-exp(2) in Figure 1). Therefore, similar to the result reported by Tatsumi, we also observe an important effect of the Si/Ti ratio on the retention of the layered MWW structure after the acid treatment and calcination.

Ti-MWW-exp(2) was further characterized by chemical analysis and UV-vis spectroscopy. This sample shows a final Si/Ti ratio of 159 in the solid (see Table 1), all of these Ti

species being in tetrahedral coordination (see the UV-vis spectrum in Figure 2).

Ar adsorption characterization of Ti-MWW-exp(1) and Ti-MWW-exp(2) can give information of zeolite pore topologies, indicating if they are more related to the MWW structure or, on the contrary, if there are differences in the pore distribution when compared to regular MWW material. As seen in Figure 3, the Ti-MWW-exp(2) material clearly presents two differentiated peaks in the curve of the pore size distribution obtained by Ar adsorption. The first peak centered at 5.3 Å is characteristic of the medium pores present in the MWW structure, whereas the peak centered at 7.3 Å can be associated with the expanded pores. Interestingly, the presence of the expanded MWW-related structure cannot be confirmed by PXRD for Ti-MWW-exp(1) (see Figure 1), but the Ar adsorption measurement indicates the appearance of expanded pores in its structure (see Figure 3).

A regular Ti-MWW material was also synthesized, and its physicochemical properties were compared with those of the Ti-MWW-exp(1) and Ti-MWW-exp(2). The typical synthesis procedure of the standard Ti-MWW zeolite combines the hydrothermal synthesis of the titanoborosilicate MWW, followed by different acid treatments to selectively remove the boron atoms.¹³ Following the synthesis described in the literature (see the Experimental Section), titanoborosilicate MWW (Ti-B-MWW) was synthesized. The PXRD pattern of this material indicates that the MWW layered precursor phase is achieved, as indicated by the 001 and 002 reflections (see Figure 1), and chemical analysis shows a molar ratio of 43 and 9.6, for Si/Ti and Si/B, respectively (see Table 1). The coordination of Ti in Ti-B-MWW has been studied by UV-vis spectroscopy, observing a very broad band in the spectrum (see Figure 2). This broad band can be assigned to the presence of tetrahedral and octahedral Ti species in the sample.

Ti-B-MWW has been acid-treated several times in order to remove most of the boron atoms, and also the octahedral Ti species. After three acid washes with nitric acid, the sample was calcined at 550 °C. This calcined sample has been named "Ti-MWW". As seen in Table 1, a large part of the boron has been removed (Si/B > 500), and the final Si/Ti molar ratio is 68. Moreover, the UV-vis spectrum of this acid-treated and calcined sample indicates that only Ti species in tetrahedral coordination remain in the solid (see Figure 2). The PXRD pattern of Ti-MWW is typical of the MWW structure, showing a very similar PXRD pattern to that of the Ti-MWW-exp(1) material. However, the Ar adsorption measurement on Ti-MWW reveals a single peak in the pore size distribution centered at 5.3 Å, characteristic of the medium-pore MWW material. This result shows the different textural properties of Ti-MWW-exp(1) synthesized following the methodology described in the present paper when compared to the regular Ti-MWW. These changes in pore size distribution should have a positive effect on molecular diffusion and site accessibility

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when reacting larger molecules, hopefully offering improved catalytic properties in selective oxidation reactions.

At this point, we have three different titanosilicate forms of MWW-related materials. On one hand, there is regular Ti-MWW and expanded Ti-MWW-exp(1); both show a similar Ti content (see Table 1), all Ti species being in tetrahedral coordination (see Figure 2), and comparable crystal sizes (see images of scanning electron microscopy, SEM, in Figure 4). The main difference between these materials is the pore size distribution obtained by Ar adsorption (see Figure 3). On the other hand, Ti-MWW-exp(2) shows a lower Ti content than the above described materials, but a better expanded layered structure, as observed by PXRD and Ar adsorption.

The low activity observed when medium-pore titanosilicates, such as MWW, are applied as catalysts in the epoxidation of cyclohexene has been well-described.^{17,18} Thus, the higher pore size distribution in the case of Ti-MWW-exp(1) and Ti-MWWexp(2) should improve the catalytic properties of Ti-MWW when a cycloalkene, such as cyclohexene, is used as a substrate in selective epoxidation. Catalytic tests on cyclohexene with MWW-related materials were performed using H_2O_2 as oxidant and acetonitrile as solvent at 333 K. As observed in Figure 5, Ti-MWW-exp(1) and Ti-MWW, both presenting similar Ti contents, behave differently on cyclohexene epoxidation. Ti-MWW-exp(1) shows a much higher activity than regular Ti-MWW, which can be easily explained by the reduction of diffusion problems due to the increase of the pore size distribution on Ti-MWW-exp(1). Indeed, the highly expanded Ti-MWW-exp(2) material shows the higher activity per active site (TOF, turnover frequency number calculated from initial reaction rates) of all studied MWW-related materials (see Table 2). In terms of cyclohexene epoxide selectivity, Ti-MWWexp(1) and Ti-MWW-exp(2) perform very well, showing values higher than 90% toward the desired epoxide molecule (see Table 2).

4. CONCLUSIONS

A new synthetic route starting from an all-silica precursor, ITQ-1, is used for the preparation of an expanded titanosilicate form of MWW-related material. This methodology improves the synthetic route reported by Tatsumi et al., where borosilicate MWW precursors, and, consequently, several postsynthetic acid treatments for removing boron atoms from the framework, were required in the synthesis of the expanded Ti-YNU-1. The expanded titanosilicate MWW-related materials prepared following the methodology presented here improve the activity of bulky cycloalkenes, such as cyclohexene, in the selective epoxidation reaction with H_2O_2 as oxidant when compared to regular Ti-MWW. This methodology could open an interesting synthesis route using pure silica layered materials, delaminated zeolites, or nanosheets as precursors for the preparation of metallosilicates.

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Author Contributions

[†]The paper was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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