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MWW-Type Titanosilicate

Synthesis, Structural Modification and Catalytic Applications to Green Oxidations

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Preface

The discovery of titanosilicates opens up new possibilities of developing heterogeneous catalytic processes for selective oxidation reactions, which has made a breakthrough in the area of zeolite materials and catalysis. Although the first generation of titanosilicate TS-1 dates back to almost 30 years ago, the research activities are still being continued worldwide in design and synthesis of novel titanosilicates, insight into active sites as well as developing practically useful catalytic technologies. In this sense, a series of titanosilicates differing in crystalline structure and pore dimension have been synthesized successfully. Particular efforts have been devoted to searching for the oxidation catalysts which have larger pore dimensions useful to process bulky molecules. Derived from lamellar precursors, so-called layered zeolites are constructing an important family in zeolite materials. Different from those with three-dimensional crystalline structures already formed in hydrothermal synthesis, the layered zeolites possess structural diversity and their structures are mendable by post modification.

Focusing on recent research advances in a new generation of titanosilicate Ti-MWW that comes from a lamellar precursor, this monograph consists of five chapters. Chapter 1 introduces briefly the catalytic features and research progress of titanosilicate catalysts. Chapter 2 describes the methods for the preparation of Ti-MWW, including hydrothermal synthesis and post isomorphous substitution route either in the presence or absence of boric acid. Chapter 3 figures out the structural modifications of Ti-MWW, full or partial delamination, and interlayer pore expansion by, silylation or pillaring techniques. Chapter 4 deals with potential catalytic applications of thus developed catalysts to innovative selective oxidations including epoxidation of various alkenes and ammoximation of ketones to oxime. Chapter 5 gives the prospects for the development and application of Ti-MWW zeolite in future. The contents range from fundamental knowledge to practically usable techniques that have been established on this specific titanosilicate.

It is our great pleasure working in this research area with many excellent experts and students from both China and Japan. We would like to sincerely thank professors Takashi Tatsumi, Tatsuaki Yashima and Takayuki Komatsu

(Tokyo Institute of Technology, Japan), Osamu Terasaki (Stockholm University, Sweden) and Dr. Weibin Fan (Chinese Academy of Science, China) for their fruitful collaboration. Many students from East China Normal University, China and Yokohama National University, Japan have made great contributions to this research subject. Without their hard work and effort, it would have been impossible to put the independent topics together.

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Contents

Chapter 1
Introduction

Zeolites are a class of crystalline aluminosilicates and silicalites with the silicon and aluminum cations tetrahedrally linked by the oxygen bridges in the framework, and then three-dimensional (3D) networks are constructed to form the channels, pores, cages, and cavities [1]. Zeolites thus possess well-defined crystalline structures as well as the textural properties of high specific surface area and high adsorption capacity. The pore windows and channels of zeolites are closely related to their well-defined crystalline structures, and usually their sizes are of molecular dimensions in the micropore region [2]. This kind of unique porosity endows zeolites with molecule sieving abilities for discriminating guest molecules and separating reactants/products. Even strong electric fields are possibly generated within zeolite pores, and as heterogeneous catalysts, zeolites then may exhibit strong quantum effects in combination with the molecular confinement of micropores [3, 4].

The chemical compositions of the zeolite frameworks are changeable and amendable, not only in the silicon to metal ratios but also in the types of coordinated metal ions. The Si/Al ratio could be varied in the range of one to infinite, whereas the transition metals and the elements other than Si and Al are also incorporated into the zeolite framework via isomorphous substitution, e.g., P [5], B [6], Ga [7], Fe [8], Ti [9], Sn [10], Ge [11], Zr [12], and V [13], etc., giving rise to so-called metallosilicates. This widens significantly the application range of zeolites as multifunctional catalysts.

Zeolites in aluminosilicate forms have long been used as solid–acid catalysts in petrochemical industry. For example, Faujasite Y (with a structure code of FAU, recognized by International Zeolite Association, IZA) is widely used as fluid catalytic cracking (FCC) catalyst, replacing conventional amorphous silica-alumina catalysts [14–16]. This opened the door for perhaps the biggest revolution in oil refining industry. Thereafter, the well-known pentasil aluminosilicate ZSM-5 with the MFI topology [17], developed in 1970s by Mobil (now known as ExxonMobil), is a versatile shape-selective catalyst in petrochemical processes for producing high valuable aromatics, e.g., *para*-xylene [18].

In 1983, Taramasso et al. [19] from Enichem group envisaged the first titanosilicate with the Ti cations isomorphously substituted in the MFI-type

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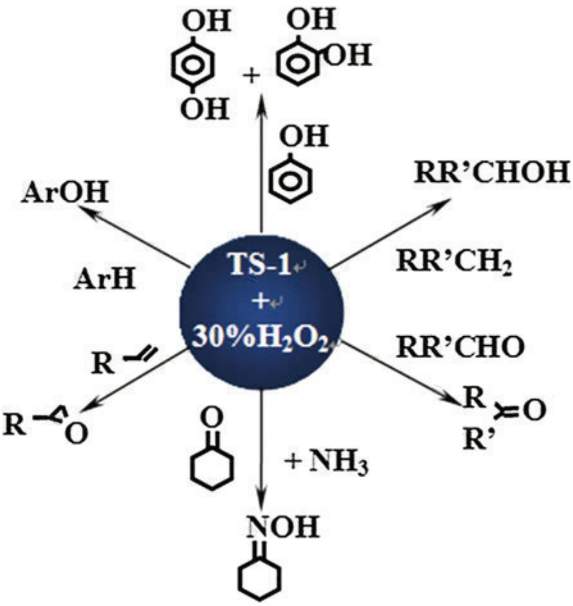


Fig. 1.1 Liquid-phase oxidation reactions based on TS-1/H_2O_2 system

silicalite-1, which is well known as TS-1. Combining the hydrophobic feature in aqueous solution and the unique porosity of the MFI framework, those isolated tetrahedral Ti sites in TS-1 can activate hydrogen peroxide molecules under relatively mild conditions (generally <373 K and 1 atm), and as shown in Fig. 1.1, they are capable of catalyzing the selective oxidation reactions of a variety of substrates [20, 21]. These reactions give water as the sole byproduct. Two world-scale processes, cyclohexanone ammoximation [22] and propylene epoxidation [23], have now been commercialized based on the TS-1/H_2O_2 catalytic system. These processes are environmentally benign in terms of greenness and zero waste disposal. Expanding the catalytic applications of zeolites from solid–acid catalysis to redox field, the great success of TS-1 is considered as the third milestone in zeolite catalysis after Y and ZSM-5 zeolites.

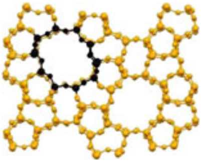
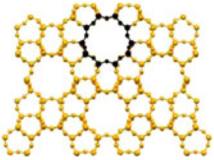
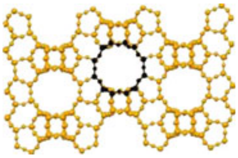
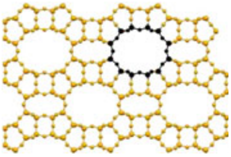
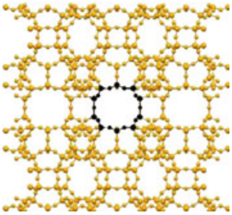
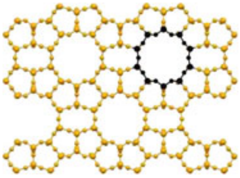
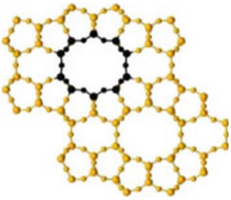
The discovery of TS-1 has encouraged the researchers to develop other titanosilicates with different zeolite structures [24–49], especially those with larger porosities and high cost performance, because TS-1 encounters some shortcomings. TS-1 is less active to the bulky and cyclic molecules owing to diffusion hindrance imposed by its medium pores of 10-membered ring (MR). TS-1 always prefers a protic solvent like methanol, which causes the solvolysis of the epoxides in alkene epoxidation, lowering the selectivity to desirable products [50]. From the viewpoint of industrial applications, TS-1 still suffers a high cost of catalyst manufacturing because it requires the use of expensive tetrapropylammonium hydroxide (TPAOH) as structure-directing agent (SDA) and organic silica source of tetraethylorthosilicate (TEOS). To be active enough, the hydrothermally synthesized crystals of TS-1 needs to be of nanosized order. This then induces separation difficulties either in catalyst preparation procedure or in catalytic processes.

In this sense, taking full use of established zeolite preparation techniques such as hydrothermal synthesis (HT), post-synthesis (PS), dry-gel conversion (DGC) [51], fluoride method [52], crystallization-promoting agent or additive-assisted method [27], a series of titanosilicates have been developed. Table 1.1 lists the representative titanosilicates prepared by various techniques together with their crystalline and pore structures. In addition to microporous titanosilicates, many Ti-containing mesoporous materials with much larger nanopores have also been reported, such as Ti-MCM-41, Ti-SBA-15, and Ti-MCM-48 [53–56]. However, they are not effective for liquid-phase oxidation with aqueous H_2O_2 as oxidant because of an extremely high hydrophilicity related to abundant surface silanol groups.

Among the microporous titanosilicates developed so far, Ti-MWW with the MWW topology [33, 38, 57], has been proved to be unique in pore structure, preparation method, oxidation activity and selectivity. MWW zeolite possesses a unique pore structure of 12-MR side cups on the crystallites exterior as well as two independent 10-MR channel systems; one contains 12-MR supercages and the other is of sinusoidal tortuosity (Fig. 1.2) [58]. As the MWW zeolite derives from a so-called MWW lamellar precursor through the dehydroxylation between the layers upon calcination, it has structural diversity, e.g., conversion to a hybrid micro-mesoporous material by intercalating [59], fully or partially delamination into thin sheets with highly accessible external surface [60, 61], or structural transfer to interlayer-expanded zeolite structure by silylation with monomeric or dipodal silanes [62–64]. This would make MWW-based catalysts find much wider applications.

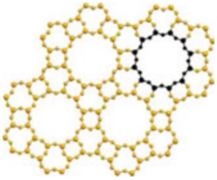
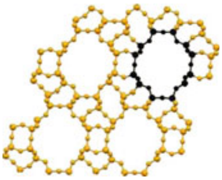
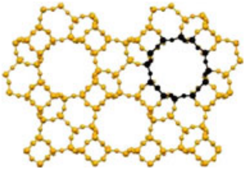
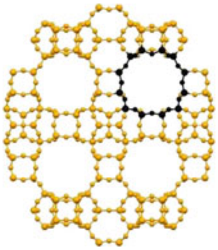
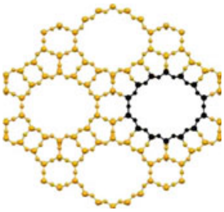
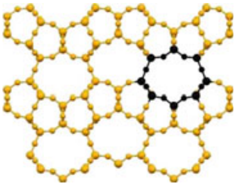
Although MWW aluminosilicate (generally known as MCM-22) is hydrothermally synthesized without difficulty, the synthesis of MWW titanosilicate (Ti-MWW) has been a challenge until we found that Ti could be effectively incorporated into the MWW framework when boric acid coexists with it in the synthesis media [33]. Making good use of structural characteristics of MWW zeolite, we have also established an original post-synthesis method for preparing boron-free Ti-MWW [38], and further converted it into a novel catalyst with more accessible active sites to bulky molecules. This book summarizes our recent works on preparing such novel titanosilicates and their catalytic properties in liquid-phase epoxidation of various alkenes as well.

Table 1.1 List of representative titanosilicates: crystalline structure, pore system and synthesis methods

Titanosilicate	Structure code	Pore channels (MR)	Synthesis method	Framework	References
TS-1	MFI	10-10	HTS, PS		[19]
TS-2	MEL	10-10-10	HTS		[24]
Ti-Beta	*BEA	12-12-12	HTS, F^-		[25–29]
Ti-MOR	MOR	12-8	PS		[30–32]
Ti-MWW	MWW	10-10 12 supercage	HTS, PS, DGC, F^-		[33–40]
Ti-ZSM-48	*MRE	10	HTS		[41]
Ti-FER	FER	10-8	HTS		[42]

(continued)

Table 1.1 (continued)

Titanosilicate	Structure code	Pore channels (MR)	Synthesis method	Framework	References
TAPSO-5	AFI	12	HTS		[43]
Ti-ZSM-12	MTW	12	HTS		[44]
Ti-MCM-68	MSE	12-10-10	PS		[45]
Ti-ITQ-7	ISV	12-12-12	HTS		[46, 47]
Ti-UTD-1	DON	14	HTS		[48]
Ti-CDS-1	CDO	10-8	HTS		[49]

HTS hydrothermal synthesis, *DGC* dry gel conversion, *PS* postsynthesis, *F*$^-$ fluoride media method

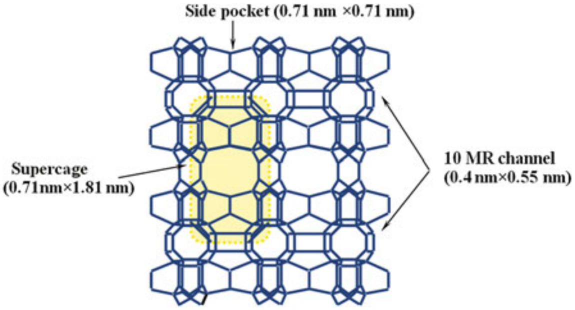


Fig. 1.2 Topology of MWW zeolites (*h0l* plane)

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