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A Career in Catalysis: Takashi Tatsumi

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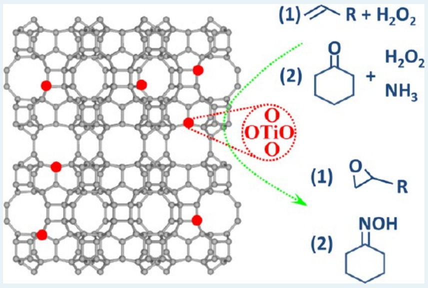

ABSTRACT: On the occasion of Professor Takashi Tatsumi's retirement and winning of the Alwin Mittasch Prize, some of his main achievements in zeolite catalysis are summarized, with a focus on the design, synthesis, and catalytic application of new titanosilicate catalysts. He and his co-workers succeeded in the direct synthesis of the MWW-type titanosilicate, Ti-MWW, by employing boric acid in the synthesis and thereafter developed a dry gel conversion method for boron-reduced Ti-MWW as well as a secondary isomorphous substitution route for boron-free Ti-MWW molecular sieves. In particular, the postsynthetic conversion involved a reversible structure interchange between three-dimensional silicalite and a two-dimensional layered precursor. Taking advantage of the structural diversity of the layered MWW zeolite precursor, phase-delaminated Ti-MMW and interlayer expanded Ti-MWW were also prepared. Using hydrogen peroxide as an oxidant, the Ti-MWW/H_2O_2 system was highly efficient for liquid-phase oxidation of a variety of substrates, particularly the epoxidation of alkenes and ammoximation of ketones. Some of the Ti-MWW-catalyzed reactions have already led to or are becoming practical catalytic technologies in industrial practice. Several other recent achievements in the synthesis and catalytic applications of other titanosilicates, zeolitic hydrid materials, and solid acid zeolite catalysts are also briefly summarized.

KEYWORDS: *zeolite, titanosilicate, aluminosilicate, MWW topology, selective oxidation, methanol to olefins, hydrocarbon cracking*

1. INTRODUCTION

The year 2013 was the occasion of the 100th anniversary of the first ammonia synthesis plant in the world beginning operation in Oppau in southwest Germany in 1913. This synthesis method is the called Haber–Bosch process, with the Nobel Prize in Chemistry awarded to Fritz Haber in 1918 and Carl Bosch in 1931, respectively, in recognition of this catalyst and technology.[1] Bosch pioneered the processing by a high-pressure chemical method, and Haber established the ammonia synthesis method based on research on the equilibrium theory of the three elements of nitrogen, hydrogen, and ammonia.

The optimized catalyst first consisted of iron and additives, including potassium and alumina. It is quite surprising that catalysts including these three elements are still used today in most ammonia synthesis plants in the world operating the Haber–Bosch process. Alwin Mittasch (1869–1953) played a key role in developing this catalyst after he tested more than 2,500 different catalyst compositions in generating the eventual, practical catalyst. The Alwin Mittasch Prize was established as a tribute to his great achievement.

In 2012, Takashi Tatsumi was honored with the Alwin Mittasch Prize, which he shared with Graham Hutchings, for his pioneering work discovering a new Ti-zeolite catalyst. Especially noteworthy is the fact that he is the first non-European winner.

Professor Tatsumi, born in Osaka, Japan in 1948, received bachelor and master degrees in 1970 and 1972, respectively, from the University of Tokyo. He received his Ph. D. in 1981 when he was a research associate at the University of Tokyo. After spending 1981–1982 as a visiting research associate at Texas A&M University with Prof. Jack H. Lunsford, he became an associate professor at the University of Tokyo in 1988. At that time, his scientific interest was gradually moving from his former field of homogeneous catalysts, that is, organometallic complex catalysts, toward solid catalysts, such as zeolites and related materials. His first research target was titanosilicates, such as TS-1, Ti-Beta, and sometimes mesoporous materials such as Ti-MCM-41. During this time, he published a nice

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sequence of papers, including some describing the efficient oxidation of alkanes and alkenes catalyzed by titanosilicates. In 1998, he was promoted to full professor of Yokohama National University and started a series of work on Ti-MWW-type catalysts, ZOL (zeolite with organic groups as lattice) materials, and chiral mesoporous materials. In 2005, he became a professor of the Tokyo Institute of Technology (Chemical Resources Laboratory) and started additional important research work there, including the development of solid acid zeolite catalysts as well as zeolite catalysts via an organic structure-directing agent (OSDA)-free synthesis route, until his retirement in March, 2013. He is a recipient of four major Japanese Awards in this field: the Catalysis Society of Japan Award (2003), the Ministry of Education, Culture, Sports, Science and Technology Award (2005); the Japan Petroleum Institute Award (2006); and the Chemical Society of Japan (CSJ) Award (2007). He has served as a president/chairman of the Catalysis Society of Japan, the Japan Petroleum Institute, and the Japan Association of Zeolites.

In this article, we briefly describe his main catalytic achievements in his scientific career (of more than 400 original papers), focusing on selected parts of the above-mentioned research topics chronologically.

2. MFI-TYPE TITANOSILICATE (TS-1)

In the 1980s, the researchers of ENI, Italy devoted themselves to the preparation and calatlytic applications of titanosilicate catalysts by isomorphous substitution of titanium active sites in the framework of the silicalite molecular sieve. They patented the first titanosilicate with the MFI topology,[2] denoted as TS-1, which is structurally analogous to the well-known ZSM-5 aluminosilicate. TS-1 was gradually proven to be an important environmentally benign, selective oxidation catalyst in combination with hydrogen peroxide as an oxidant for a variety of substrates, producing only water as a byproduct.[3] With a strong background in liquid-phase homogeneous oxidation reactions, Tatsumi paid great attention to the development of the TS-1/H_2O_2 system and started his research on alkane oxidation over TS-1 using H_2O_2 with his Ph.D. student (Dr. Nakamura) in 1988. Since most Japanese researchers utilized only commercially available zeolites at the time, he was one of the pioneers in Japan at synthesizing zeolites in his own lab. That was the beginning of a significant research direction shift, as well as, henceforth, several great successes in zeolite catalysis.

Alkane oxidation worked with the TS-1/H_2O_2 system to give the corresponding ketones and alcohols under mild conditions. The results were reported in 1990;[4] only 1 month after his publication, Jacobs et al. published similar results in *Nature*.[5] As the number of citations of Tatsumi's articles increased fast, he realized the importance and impact of titanosilicates, which led him into the exciting field of the design and preparation of porous titanosilicates, naturally pursuing their catalytic applications in liquid-phase selective oxidation reactions, as well. Thus, his interest in titanosilicate catalysts gradually became his life's work, and he began addressing the challenge of developing alternate framework structures.

3. MWW-TYPE TITANOSILICATE (TI-MWW)

3.1. Synthesis of Ti-MWW.

The discovery of TS-1 opened the new possibility of developing environmentally benign oxidation processes based on zeolite catalysts. Its successful application to the commercial processes for manufacturing bulk chemicals of ε-caprolactam and propylene oxide (PO) marked a new milestone in zeolite catalysis. This stimulated Tatsumi to prepare new titanosilicates structurally different from TS-1, for example, hydrothermally synthesized Ti-SAPO-37[6] and Ti-Beta,[7,8] by dry gel conversion methods. Meanwhile, he grew aware that the MWW framework, with its unique channel system, known as MCM-22 in aluminosilicate form,[9] was suitable for designing more effective oxidation catalysts, and he began to work on the preparation of the corresponding titanosilicate in 1997.

The MWW-type zeolites were originally synthesized as PSH-3 (Sued Chemie),[10] SSZ-25 (Chevron),[11] ERB-1 (Eni),[12] and MCM-22 (Mobil).[9] Taking advantage of the synthetic system for the B-containing MWW zeolite ERB-1,[13] Tatsumi and co-workers succeeded in hydrothermally synthesizing Ti-MWW for the first time (Figure 1).[14,15] Using boric acid as a so-called structure-supporting agent, Ti-MWW was crystallized readily in the absence of alkali cations, which is also a highly preferred condition to avoid the poisoning of Ti active sites in titanosilicates. More importantly, they disclosed that handling the Ti-MWW precursor by conventional calcination procedures led to only a low activity catalyst, whereas an acid treatment on the as-made precursor first, followed by calcination, gave rise to a highly active catalyst for the liquid-phase epoxidation of alkenes with H_2O_2. It was also critical to selectively remove the extraframework Ti species together with a part of the framework boron to prepare active Ti-MWW.[15]

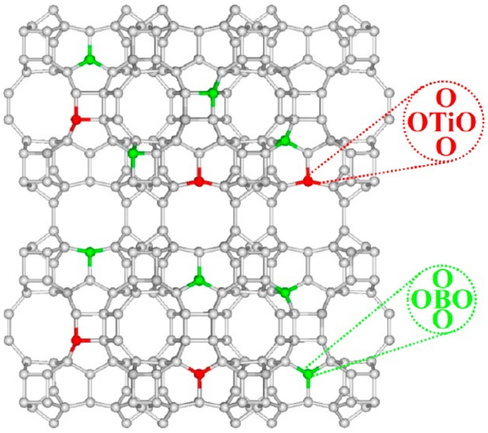

Figure 1. The structure of Ti-MWW synthesized in a boric acid system.

Thereafter, Tatsumi and his co-workers made a great effort to reduce or eliminate the boron species that are unnecessary in terms of oxidation catalysis. In this sense, boron-reduced Ti-MWW has been prepared by a dry gel conversion method under conditions in which the boron content was reduced by ~90%.[16]

The postsynthetic incorporation of Ti in the borosilicate zeolites (Beta and SSZ-33) after deboronation has been applied by other laboratories to synthesize B-free Ti-containing zeolites, as well.[17,18] Parallel to direct synthesis, a novel postsynthesis method was proposed to prepare boron-free Ti-MWW with more active Ti sites. Ti-free MWW borosilicate was first synthesized, and then deboronated by repeated calcination and acid-treatment procedures. B-free Ti-MWW was then obtained by hydrothermally treating the resultant B-free MWW silicalite in a mixture of a Ti source and piperidine or hexametheleneimine (two typical SDAs for crystallizing the MWW zeolites).[19] Unlike conventional methods, this postsynthesis approach involved a reversible structural interchange between a 3-dimensional (3D)

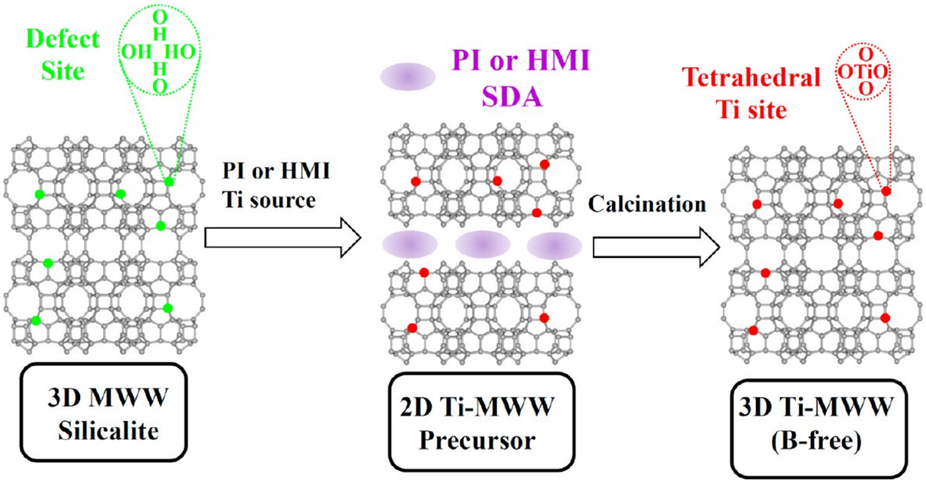

Figure 2. Postsynthesis of B-free Ti-MWW through a reversible 3D ↔ 2D structure interchange.

zeolite and a 2-dimensional (2D) layered precursor with simultaneous Ti incorporation into the defect hydroxyl nests (Figure 2). This strategy not only is useful for preparing highly active Ti-MWW catalysts, but also suggests that the 3D MWW zeolite structure is not as rigid as imagined.

The pioneering research concerning the preparation of Ti-MWW laid the foundation for thereafter developing boron-less Ti-MWW using designed linear quaternary ammonium cations as SDA[20] or B-free Ti-MWW using dual templating agents by direct hydrothermal synthesis.[21]

3.2. Catalytic Properties of Ti-MWW. A number of titanosilicates have been developed since TS-1, but frankly speaking, they were generally intrinsically less active than TS-1 in selective oxidation reactions such as alkene epoxidation and ketone ammoximation if the substrate molecules do not suffer diffusion limitation and hindrance inside the zeolite channels. Tatsumi and his co-workers found that Ti-MWW was more active than TS-1 in the epoxidation of linear alkenes using H_2O_2 as the oxidant. Ti-MWW efficiently catalyzed the epoxidation of 1-hexene,[22,23] allyl alcohol,[24] diallyl ether,[25] and allyl chloride,[26] giving the corresponding epoxides usually with >99% selectivity.

Possessing both open reaction spaces of intracrystal 12-mermbered ring (MR) supercages and a 12-MR side cup on the exterior surface, Ti-MWW also showed the advantages in the oxidation of cyclic molecules with relatively bulky dimensions, for example, in the epoxidation of cyclohexene[22,23] and cyclopentene[27] and 2,5-dihydrofuran,[28,29] and in the oxidation of amines,[30] 1,4-dioxane,[31] and sulfides.[32] A comprehensive investigation has been made into the shape-selectivity of the MWW channels and the contribution of existing location-dependent Ti active sites in these reactions.

It is noteworthy that with respect to alkene epoxidation, the developed Ti-MWW material proved to be a promising catalyst for producing propylene oxide (PO) via direct epoxidation of propylene using hydrogen peroxide as an oxidant. Preferring an inert solvent of acetonitrile rather than the protic methanol required by TS-1, Ti-MWW is capable of providing a high propylene conversion at >99% PO selectivity.[33] This attracted the attention of commercial chemical makers, such as Sumitomo and BASF, for the purpose of developing innovative PO manufacturing processes.[34,35]

Tatsumi and his co-workers also found a unique trans selectivity of Ti-MWW in the epoxidation of *cis*/*trans*-alkenes with hydrogen peroxide. TS-1 has been used to produce the epoxy derivatives with cis configuration in the epoxidation of a mixture of containing cis/trans alkene isomers.[36] This is attributed to the notion that the cis isomer, with a relatively larger molecular size, presumably is less reactive than the trans isomer. In contrast, in the case of Ti-MWW, the catalytic feature in the epoxidation of olefinic stereoisomers is totally opposite.[37,38] Ti-MWW exhibits a singularity never previously observed on conventional titanosilicates in that it selectively epoxidizes the trans isomer to give a selectivity of ~80% for the corresponding trans epoxide from an alkene mixture with a cis/trans ratio of 50:50. This kind of unique shape selectivity has been assumed to be closely related to the sinusoidal shape of the 10-MR channels in Ti-MWW.

In addition to alkene epoxidation, Ti-MWW was also found to be an important catalyst for the liquid-phase ammoximation of ketones to the corresponding oximes with ammonia and hydrogen peroxide. Compared with TS-1 and other titanosilicates, Ti-MWW catalyzed highly effectively or even more actively the ammoximation of cyclohexanone or methyl ethyl ketone, giving ketone or aldehyde conversions and the corresponding oxime selectivity over 99% under optimized conditions.[39−42] With respect to the ammoximation of linear ketones such as methyl ethyl ketone, Ti-MWW was particularly superior to TS-1 in methyl ethyl ketone oxime selectivity.[43] Ti-MWW totally avoided the overoxidation of methyl ethyl ketone to 2-nitrobutane, whereas TS-1 may produce 2-nitrobutane up to 20%. The ammoximation technique based on Ti-MWW catalyst has led to a commercial process for manufacturing methyl ethyl ketone oxime with a capacity of 15 000 tons/year in China. Ti-MWW thus became the second titanosilicate after TS-1 finding practical use in industry, although TS-1 is still an industrial standard catalyst for oxidation reactions.

The systematic research focusing on the synthesis and catalytic applications of Ti-MWW have established a new catalytic system for liquid-phase oxidations, in which Ti-MWW is capable of giving substrate conversions as high as 95%, desirable product selectivity >99%, as well as hydrogen peroxide utilization efficiency over 90% (Figure 3). Complementing the strengths of TS-1, Ti-MWW is expected to further open up a variety of greener oxidation processes in the petrochemical industry.

3.3. Structural Modification of Ti-MWW. Taking full advantage of the diversity of layered MWW zeolites, Tatsumi and his co-workers have further carried out the structural modification of Ti-MWW for the purpose of enhancing the catalytic activity of Ti-MWW as well as its applicability to the

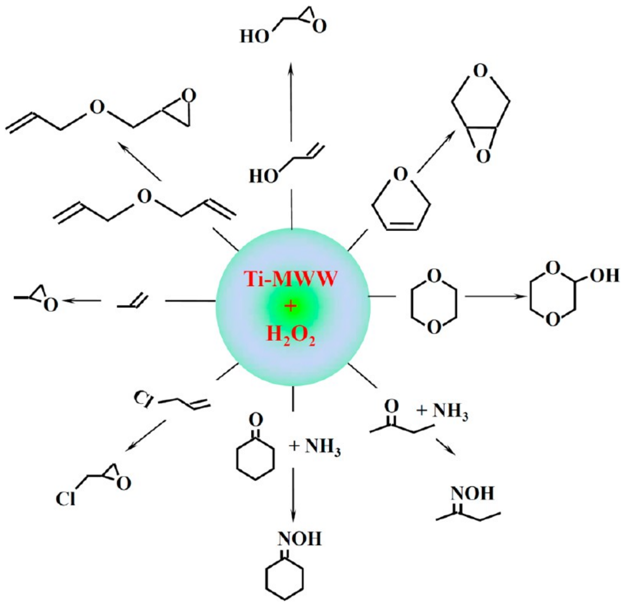

Figure 3. Selective oxidation reactions catalyzed by the Ti-MWW/H_2O_2 system.

oxidation of bulky molecules (Figure 4). Following well established delamination procedures developed on MCM-22 aluminosilcates,[44] Ti-MWW was fully delaminated by combining surfactant-assisted preswelling and subsequent ultrasonic treatment (Figure 4).[45,46] The resultant Del-Ti-MWW was essentially composed of a collection of MWW thin sheets (Figure 5) possessing a doubled specific surface area in comparison with pristine Ti-MWW, and the material exhibited greatly enhanced activity in the epoxidation of alkenes ranging from linear to cyclic structures with increasing carbon numbers.

To open the reaction space of Ti-MWW, a partial delamination technique has also been developed by removing partially the interlayer pillaring SDA species and then disturbing the ordered stacking and array of the MWW sheets. The resultant Ti-MCM-56, with a structure that is analogous to hydrothermally synthesized MCM-56 aluminosilicate, was shown to be more active than Ti-MWW in the oxidation of bulky molecules.[47]

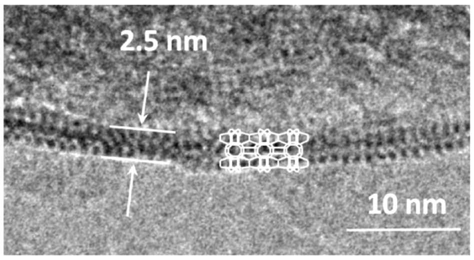

Figure 5. High-resolution TEM image of a single sheet in Del-Ti-MWW.[46]

Tatsumi and his co-workers have also discovered a new titanosilicate, Ti-YNU-1,[48] which was named after Yokohama National University, where he worked as a full professor from 1998 to 2005. Ti-YNU-1 has a new type of zeolite topology with 12-MR pores between the MWW layers, which could be formed by the expansion of the 10-MR pores in Ti-MWW (Figure 6).[48,49] This kind of interlayer-expanded structure was assumed to be constructed by pillaring with the silica debris dissolved from the crystal during the acid treatment. Tatsumi and his co-workers proposed a more general and feasible methodology for design and synthesis of interlayer expanded zeolites (IEZs) through silylating the zeolitic layered precursors with a monomeric silane.[50] In addition to IEZ-Ti-MWW, this method worked well in building a variety of zeolite structures with larger pores. Starting from layered precursors of MCM-22(P),[50] PREFER,[51] RUB-39,[52] RUB-36,[53] and PLS-4,[54] new zeolitic structures with well ordered and enlarged pores have been obtained successfully by interlayer silylation. Thus, the chemistry developed by Tatsumi substantially contributed to the emerging so-called two-dimensional zeolite chemistry[55] and the successful synthesis of new zeolites, IPC-2 and IPC-4.[56]

4. TITANOSILICATE MATERIALS TO THE FUTURE

The preparation, structural modification, and catalytic applications of Ti-MWW and related titanosilcates have been one of Tatsumi's major research topics in the past decade. Tatsumi has devoted himself almost exclusively to the study of

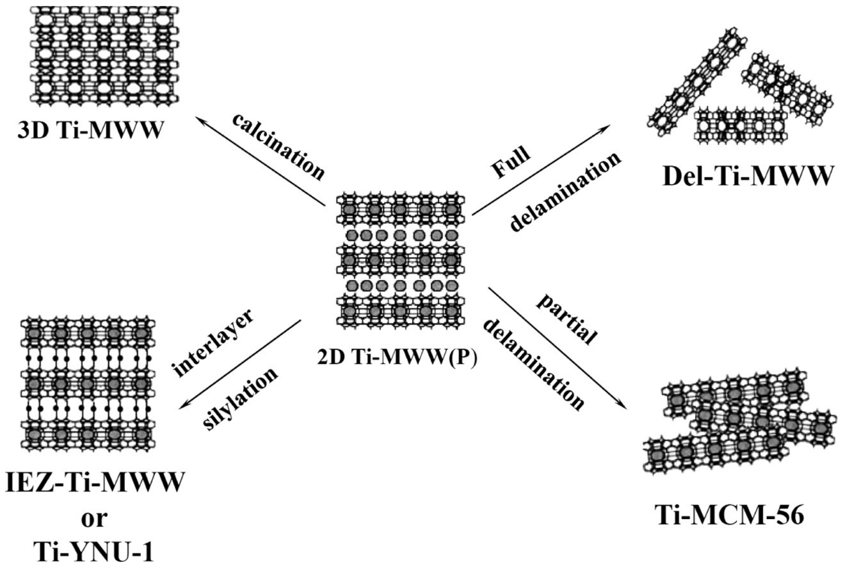

Figure 4. Structural modification of Ti-MWW by post treatments.

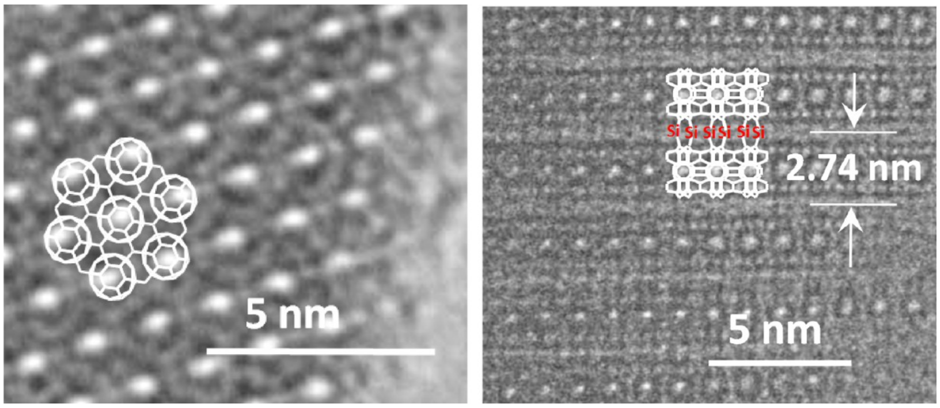

Figure 6. Edge-on TEM images of Ti-YNU-1 taken along the [001] incidence (left) and [001] incidence (right).[48,49]

the improvement of TS-1 in recent years. In 2008, Tatsumi and his co-workers developed a method for preparing Ti-rich TS-1 free of extra-framework Ti species by crystallizing TS-1 in the presence of $(NH_4)_2CO_3$, which has been named the "YNU method".[57] Of course, beyond this, he has also made an impact in several other segments of materials synthesis and catalysis. For example, he has also prepared other titanosilicate oxidation catalysts, new organozeolite materials, and tailored mesostructured materials. Ti-MCM-68 has been developed by a postsynthesis method through gas−solid reaction with $TiCl_4$ vapor.[58] Ti-MCM-68 proved to be particularly active for the hydroxylation of phenol to diphenols using hydrogen peroxide. This finding covers a shortfall of Ti-MWW, which was much less active in the hydroxylation of aromatics than other titanosilicates.

5. ORGANIC−INORGANIC HYBRID ZEOLITES

Just after moving to Yokohama National University, along with his promotion to full professor in 1998, he started work developing the new functional porous materials in addition to titanosilicate materials. A great achievement was made within several years, and in 2003, Tatsumi and his co-workers published the first report of a new class of materials, coined ZOLs (zeolites with organic groups as a lattice), in which a methylene group was incorporated in the framework as a 2-connected species ($\equiv$Si-CH_2−Si$\equiv$).[59,60] ZOL materials were the first organic−inorganic hybrid composite in which an organic group was incorporated into a crystalline microporous material not as a pendant functional group but as part of the framework (Figure 7). Introducing organic groups into the framework provided the material with new functionalities in adsorption by enhancing the hydrophobicity.

6. ZEOLITE SOLID ACID CATALYST

6.1. Zeolite Catalysts for the MTO Reaction.

In 2005, Tatsumi moved to the Tokyo Institute of Technology and started several other catalytic research directions. One of them was the development of zeolite solid acid catalysts for the methanol-to-olefins (MTO) reaction, which has received great attention because of the shortage of crude oil in the foreseeable future. He improved the catalytic performance of the CHA- and MFI-type aluminosilicate zeolites by optimizing the acid properties, for example, altering the Si/Al ratio and by partial replacement of Al with B, Ga, or Fe.[61−64]

The mechanism of the initial C−C bond formation on methanol to olefin (MTO) conversion has not been clarified completely so far. In general, a hydrocarbon-pool mechanism may play a decisive role in the olefin production. Tatsumi and his co-workers also tackled the clarification of the reaction mechanism of the MTO reaction by applying various characterization techniques, such as NMR (^{27}Al, ^{29}Si, and ^{11}B)[65] and in situ IR.[66,67] They detrmined that propene was formed as an initial main product from the reaction of methoxy species with ethene, methanol or dimethylether. This finding would contribute a rationale for the synthesis strategy for alternative zeolite catalysts with improved catalytic performance.

Industrial demands for commodity chemicals are currently shifting from C2−C3 to C3−C4 olefins such as propene and butenes. Small-pore zeolites do not meet this demand, and Tatsumi and his co-workers are still continuing their research on the development of zeolite catalysts that can enhance selective production of C3−C4 olefins by conversion of methanol.

6.2. Synthesis of the RTH-Type Zeolite without Use of Organic Structure-Directing-Agents.

The RTH-type zeolite, which was discovered at 1995, consists of the RTH cages with the openings of 8-MR and has two-dimensional channels with an aperture size of 0.41 × 0.38 nm for the nondistorted 8-MR pore and 0.56 × 0.25 nm for the distorted 8-MR pore, which run parallel to the *a*-axis and the *c*-axis, respectively.[68] The RTH-type zeolite has been expected to show unique properties in the field of catalysis and adsorption because of its unique structure.[68] Tatsumi has also been interested in the RTH-type aluminosilicate zeolite as a catalyst for the MTO reaction. Unfortunately, however, only two examples of RTH-type zeolites had been reported until 2009. One is RUB-13, which is an RTH-type borosilicate and has been synthesized by using 1,2,2,6,6-pentamethylpiperidine (PMP) as the OSDA in combination with ethylenediamine (EDA).[68] The other is SSZ-50, which is the RTH-type aluminosilicate and has been synthesized in the presence of *N*-ethyl-*N*-methyl-5,7,7-trimethylazoniumbicyclo[4.1.1]octane cation as OSDA.[69] From a practical viewpoint, the use of these organic structure-directing agents (OSDA) could significantly limit their industrial applications. For this reason, the synthesis conditions and the diversification of the RTH-type zeolite had not been thoroughly investigated.

Tatsumi and his co-workers have established the method for preparing RTH-type zeolites without using any OSDAs (Figure 8).[70,71] The key points are the addition of sodium hydroxide and use of calcined [B]-RUB-13 as seeds, as well as the molar composition of water. The prepared RTH-type zeolites synthesized without any organic templates were named "TTZ-1" (Tokyo Tech Zeolite) series. Furthermore, initial

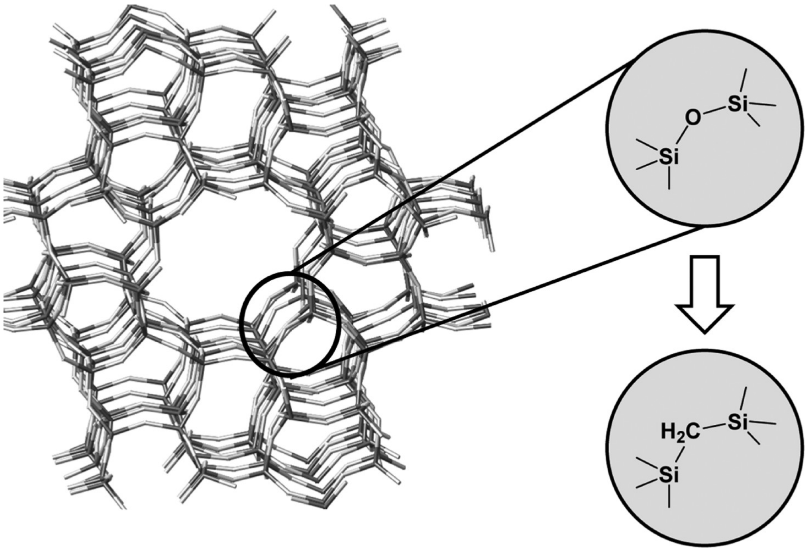

Figure 7. Structure of zeolite with organic groups as lattice.

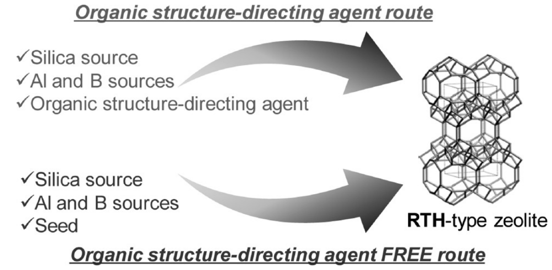

Figure 8. Preparation of the RTH-type zeolite with or without using organic structure-directing agents.

studies have demonstared that the RTH-type aluminosilicate has a high potential for the selective production of propylene through the MTO reaction.[70]

6.3. Catalytic Cracking of Naphtha over Zeolitic Solid Acid Catalysts. In 2009, Tatsumi and his colleagues in industrial and academic fields launched a national research project fully supported by the New Energy and Industrial Technology Development Organization (NEDO) to develop high-performance zeolite catalysts as well as catalytic processes that are capable of producing useful petrochemicals, such as ethylene, propylene, butenes, and BTX, from naphtha in higher yields and selectivities than the conventional thermal cracking processes.[72] To develop high-performance zeolite catalysts, Tatsumi and his colleagues have screened zeolites with various topologies to find the zeolites with outstanding catalytic properties using model molecules for naphtha. This project has found that ZSM-5 (MFI), ferrierite (FER), and MCM-68 (MSE) show relatively high activities and selectivities for the desired products. Nanosized zeolites were synthesized and put through the screening, which proved to be effective in improving the activity, selectivities, and catalyst life.[73,74] With the aims of lengthening the catalyst life and the control of the product distribution, the research continues today.

7. OTHER ACHIEVEMENTS

7.1. Mesoporous Silica Molecular Sieves. Tatsumi and his co-workers have also been highly involved in the preparation and application of mesoporous silica molecular sieves, which are potentially applied as catalysts and adsorbents for bulky reactant molecules that cannot enter into the micropores of zeolites. In 2003, Tatsumi and his co-workers developed a synthesis route for preparing mesoporous materials by using, for the first time, anionic surfactants as templates.[75−77] Utilizing this route, Tatsumi and his co-workers realized the synthesis of a chiral mesoporous silica with helical mesopores about 2.2 nm in diameter by using chiral anionic surfactants, *N*-myristoyl derivatives of L- and D-alanines.[78] The product was the first example of mesoporous materials with an obvious chirality, and this achievement was published in *Nature* in 2004.

7.2. Uniform-Sized Silica Nanospheres. Colloidal silica spheres uniform in size and shape have been widely used in industrial fields. The Stöber method is well-known to produce colloidal silica spheres by hydrolysis and condensation of silicon alkoxides (e.g., TEOS) in alcohol solvents (e.g., ethanol) in the presence of water and a base catalyst (e.g., NH_3).[79] However, this method hardly provides access to uniform-sized silica nanospheres with a size below 50 nm. In 2006, Tatsumi and his co-workers developed a simple and novel liquid-phase method for preparing uniform-sized silica nanospheres (SNSs) ~12 nm in size (Figure 9).[80,81] The fine-tuning of the size of the SNSs widely ranging from 14 to 550 nm has been attained.[82]

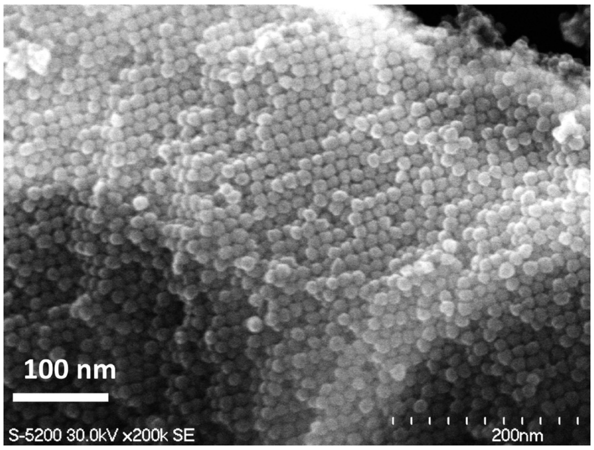

Figure 9. High-resolution scanning electron microscopic (HRSEM) image of uniformly sized silica nanospheres (SNSs) ~12 nm in size.

The colloidal crystal of the SNSs can serve as a template for fabricating mesoporous carbon and various metal oxides, as well.[83]

SUMMARY

Prof. Takashi Tatsumi has had a long and distinguished career in zeolite chemistry, catalysis, and technology. The achievements made so far have demonstrated that he is adept at carrying out fundamental studies that also impact practical applications with real engineering value. In particular, the innovative catalytic technologies obtained with Ti-MWW are bearing fruit in commercial oxidation processes. On the occasion of Tatsumi's retirement from a formal university professorship, we would like acknowledge his contribution to the zeolite and heterogeneous catalysis communities with this retrospective Account. He will continue to serve as a vice president in the Tokyo Institute of Technology and still is the head of a large project on technology innovation. We wish him good success in his new ventures.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) URL: www.nobelprize.org/nobel_prizes/chemistry/laureates/

(2) Taramasso, M.; Perego, G.; Notari, B. U.S. Patent 4,410,501, 1983.

(3) Bellussi, G.; Rigguto, M. S. *Stud. Surf. Sci. Catal.* **1994**, *85*, 177.

(4) Tatsumi, T.; Nakamura, M.; Negishi, S.; Tominaga, H. *J. Chem. Soc. Chem. Commun.* **1990**, 476.

(5) Huybrechts, D. R. C.; De Bruycker, L.; Jacbos, P. A. *Nature* **1990**, *345*, 240.

(6) Jappar, N.; Tanaka, Y.; Nakata, S.; Tatsumi, T. *Microporous Mesoporous Mater.* **1998**, *23*, 169.

(7) Jappar, N.; Xia, Q.; Tatsumi, T. *J. Catal.* **1998**, *180*, 132.

(8) Tatsumi, T.; Jappar, N. *J. Phys. Chem. B* **1998**, *102*, 7126.

(9) Leonowicz, M. E.; Lawton, J. A.; Lawton, S. L.; Rubin, M. K. *Science* **1994**, *264*, 1910.

(10) Puppe, L.; Weisser, J. U.S. Patent 4,439,409, 1984.

(11) Zones, S. I. E. Patent, 231,860, 1987.

(12) Belussi, G.; Perego, G.; Clerici, M. G.; Giusti, A. *Eur. Pat. Appl.* EPA 293032, 1988.

(13) Millini, R.; Perego, G.; Parker, W. O., Jr.; Bellussi, G.; Carluccio, L. *Microporous Mater.* **1995**, *4*, 221.

(14) Wu, P.; Tatsumi, T.; Komatsu, T.; Yashima, T. *Chem. Lett.* **2000**, 774.

(15) Wu, P.; Tatsumi, T.; Komatsu, T.; Yashima, T. *J. Phys. Chem. B* **2001**, *105*, 2897.

(16) Wu, P.; Miyaji, T.; Liu, Y.; He, M.; Tatsumi, T. *Catal. Today* **2005**, *99*, 233.

(17) Rigutto, M. S.; de Ruiter, R.; Niederer, J. P. M.; van Bekkum, H. *Stud. Surf. Sci. Catal.* **1994**, *84*, 2245−2252.

(18) Dartt, C. B.; Davis, M. E. *Appl. Catal., A* **1996**, *143*, 53−73.

(19) Wu, P.; Tatsumi, T. *Chem. Commun.* **2002**, 1026.

(20) Liu, N.; Liu, Y.; Yue, C.; Wu, H.; Li, X.; He, M.; Wu, P. *Chem. Lett.* **2007**, *36*, 916.

(21) Liu, N.; Liu, Y.; Wu, H.; He, M.; Wu, P. *Stud. Surf. Sci. Catal.* **2007**, *170*, 464.

(22) Wu, P.; Tatsumi, T.; Komatsu, T.; Yashima, T. *J. Catal.* **2001**, *202*, 245.

(23) Fan, W.; Wu, P.; Tatsumi, T. *J. Catal.* **2008**, *256*, 62.

(24) Wu, P.; Tatsumi, T. *J. Catal.* **2003**, *214*, 317.

(25) Wu, P.; Liu, Y.; He, M.; Tatsumi, T. *J. Catal.* **2004**, *228*, 183.

(26) Wang, L.; Liu, Y.; Xie, W.; Zhang, H.; Wu, H.; Jiang, Y.; He, M.; Wu, P. *J. Catal.* **2007**, *246*, 205.

(27) Wu, P.; Nuntasri, D.; Liu, Y.; Wu, H.; Jiang, Y.; Fan, W.; He, M.; Tatsumi, T. *Catal. Today* **2006**, *117*, 199.

(28) Wu, H.; Wang, L.; Zhang, H.; Liu, Y.; Wu, P.; He, M. *Green Chem.* **2006**, *8*, 78.

(29) Wu, H.; Liu, Y.; Wang, L.; Zhang, H.; He, M.; Wu, P. *Appl. Catal., A* **2007**, *320*, 173.

(30) Xie, W.; Zheng, Y.; Zhao, S.; Yang, J.; Liu, Y.; Wu, P. *Catal. Today* **2010**, *157*, 114.

(31) Fan, W.; Kubota, Y.; Tatsumi, T. *ChemSusChem* **2008**, *1*, 175.

(32) Gao, G.; Cheng, S.; An, Y.; Si, X.; Fu, X.; Liu, Y.; Zhang, H.; Wu, P.; He, M. *ChemCatChem* **2010**, *2*, 459.

(33) Song, F.; Liu, Y.; Wang, L.; Zhang, H.; He, M.; Wu, P. *Stud. Surf. Sci. Catal.* **2007**, *170*, 1236.

(34) Tsuji, J.; Yamamoto, J.; Ishino, M.; Oku, N. *Sumitomo Kagaku*, **2006**, *1*, 1. URL: http://www.sumitomo-chem.co.jp/english/rd/report/theses/docs/20060100_ely.pdf

(35) Bassler, P.; Göbbel, H.-G.; Weidenbach, M. *Chem. Eng. Trans.* **2010**, *21*, 571.

(36) Clerici, M. G.; Ingallina, P. *J. Catal.* **1993**, *140*, 71.

(37) Wu, P.; Tatsumi, T. *Chem. Commun.* **2001**, 897.

(38) Wu, P.; Tatsumi, T. *J. Phys. Chem. B* **2002**, *106*, 748.

(39) Song, F.; Liu, Y.; Wu, H.; He, M.; Wu, P.; Tatsumi. *Chem. Lett.* **2005**, 1436.

(40) Song, F.; Liu, Y.; Wu, H.; He, M.; Wu, P.; Tatsumi, T. *J. Catal.* **2006**, *237*, 359.

(41) Zhao, S.; Xie, W.; Yang, J.; Liu, Y.; Zhang, Y.; Xu, B.; Jiang, J.; He, M.; Wu, P. *Appl. Catal., A* **2011**, *394*, 1.

(42) Xu, L.; Peng, H.; Zhang, K.; Wu, H.; Chen, L.; Liu, Y.; Wu, P. *ACS Catal.* **2013**, *3*, 103.

(43) Song, F.; Liu, Y.; Wang, L.; Zhang, H.; He, M.; Wu, P. *Appl. Catal., A* **2007**, *327*, 22.

(44) Corma, A.; Fornes, V.; Pergher, S. B.; Maesen, Th. L. M.; Buglass, G. *Nature* **1998**, *396*, 353.

(45) Nuntasri, D.; Wu, P.; Tatsumi, T. *Chem. Lett.* **2003**, *32* (4), 326.

(46) Wu, P.; Nuntasri, D.; Ruan, J.; Liu, Y.; He, M.; Fan, W.; Terasaki, O.; Tatsumi, T. *J. Phys. Chem. B* **2004**, *108*, 19126.

(47) Wang, L.; Wang, Y.; Liu, Y.; Chen, L.; Cheng, S.; Gao, G.; He, M.; Wu, P. *Microporous Mesoporous Mater.* **2008**, *113*, 435.

(48) Fan, W.; Wu, P.; Namba, S.; Tatsumi, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 236.

(49) Ruan, J.; Wu, P.; Slater, B.; Terasaki, O. *Angew. Chem., Int. Ed.* **2005**, *44*, 6719.

(50) Wu, P.; Ruan, J.; Wang, L.; Wu, L.; Wang, Y.; Liu, Y.; Fan, W.; He, M.; Terasaki, O.; Tatsumi, T. *J. Am. Chem. Soc.* **2008**, *130*, 8178.

(51) Ruan, J.; Wu, P.; Slater, B.; Zhao, Z.; Wu, L.; Terasaki, O. *Chem. Mater.* **2009**, *21*, 2904.

(52) Tijsebaert, B.; Henry, M.; Gies, H.; Xiao, F.; Zhang, W.; Bao, X.; Imai, H.; Tatsumi, T.; Muller, U.; Yilmaz, B.; Jacobs, P.; De Vos, D. *J. Catal.* **2011**, *282*, 47.

(53) Xiao, F.; Xie, B.; Zhang, H.; Wang, L.; Meng, X.; Zhang, W.; Bao, X.; Yilmaz, B.; Muller, U.; Gies, H.; Imai, H.; Tatsumi, T.; De Vos, D. *ChemCatChem* **2011**, *3*, 1442.

(54) Xu, H.; Yang, B.; Jiang, J.; Jia, L.; He, M.; Wu, P. *Microporous Mesoporous Mater.* **2013**, *169*, 88.

(55) Roth, W. J.; Čejka, J. *Catal. Sci. Technol.* **2011**, *1*, 43−53.

(56) Roth, W. J.; Nachtigall, P.; Morris, R. E.; Wheatley, P. S.; Seymour, V. R.; Ashbrook, S. E.; Chlubná, P.; Grajciar, L.; Položij, M.; Zukal, A.; Shvets, O.; Čejka, J. *Nat. Chem.* **2013**, *5*, 628−633.

(57) Fan, W.; Duan, R.-G.; Yokoi, T.; Wu, P.; Kubota, Y.; Tatsumi, T. *J. Am. Chem. Soc.* **2008**, *130*, 10150−10164.

(58) Kubota, Y.; Koyama, Y.; Yamada, T.; Inagaki, S.; Tatsumi, T. *Chem. Commun.* **2008**, 6224.

(59) Yamamoto, K.; Sakata, Y.; Nohara, Y.; Takahashi, Y.; Tatsumi, T. *Science* **2003**, *300*, 470.

(60) Yamamoto, K.; Tatsumi, T. *Chem. Mater.* **2008**, *20*, 972.

(61) Zhu, Q.; Kondo, J. N.; Ohnuma, R.; Kubota, Y.; Yamaguchi, M.; Tatsumi, T. *Microporous Mesoporous Mater.* **2008**, *112*, 153−161.
(62) Zhu, Q.; Hinode, M.; Yokoi, T.; Kondo, J. N.; Kubota, Y.; Tatsumi, T. *Microporous Mesoporous Mater.* **2008**, *116*, 253−257.
(63) Zhu, Q.; Hinode, M.; Yokoi, T.; Yoshioka, M.; Kondo, J. N.; Tatsumi, T. *Catal. Commun.* **2009**, *10*, 447−450.
(64) Zhu, Q.; Kondo, J. N.; Inagaki, S.; Tatsumi, T. *Top. Catal.* **2009**, *52*, 1272−1280.
(65) Zhu, Q.; Kondo, J. N.; Tatsumi, T.; Inagaki, S.; Ohnuma, R.; Kubota, Y.; Shimodaira, Y.; Domen, K. *J. Phys. Chem. C* **2007**, *111*, 5409−5415.
(66) Yamazaki, H.; Shima, H.; Imai, H.; Yokoi, T.; Tatsumi, T.; Kondo, J. N. *Angew. Chem., Int. Ed.* **2011**, *50*, 1853−1856.
(67) Yamazaki, H.; Shima, H.; Imai, H.; Yokoi, T.; Tatsumi, T.; Kondo, J. N. *J. Phys. Chem. C* **2012**, *116*, 24091−24097.
(68) Vortmann, S.; Marler, B.; Gies, H.; Daniels, P. *Microporous Mater.* **1995**, *4*, 111−121.
(69) Lee, G. S.; Zones, S. I. *J. Solid State Chem.* **2002**, *167*, 289−298.
(70) Yokoi, T.; Yoshioka, M.; Imai, H.; Tatsumi, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 9884−9887.
(71) Yoshioka, M.; Yokoi, T.; Liu, M.; Imai, H.; Inagaki, S.; Tatsumi, T. *Microporous Mesoporous Mater.* **2012**, *153*, 70−78.
(72) URL: http://www.nedo.go.jp/introducing/iinkai/kenkyuu_bunkakai_23h_cyuukan_3_1_index.html.
(73) Mochizuki, H.; Yokoi, T.; Imai, H.; Watanabe, R.; Namba, S.; Kondo, J. N.; Tatsumi, T. *Microporous Mesoporous Mater.* **2011**, *145*, 165−171.
(74) Mochizuki, H.; Yokoi, T.; Imai, H.; Namba, S.; Kondo, J. N.; Tatsumi, T. *Appl. Catal., A* **2012**, *449*, 188−197.
(75) Yokoi, T.; Yoshitake, H.; Tatsumi, T. *Chem. Mater.* **2003**, *15*, 4536.
(76) Che, S.; Garcia-Bennett, A. E.; Yokoi, T.; Sakamoto, K.; Kunieda, H.; Terasaki, O.; Tatsumi, T. *Nat. Mater.* **2003**, *2*, 801.
(77) Garcia-Bennett, A. E.; Terasaki, O.; Che, S.; Tatsumi, T. *Chem. Mater.* **2004**, *16*, 813.
(78) Che, S.; Liu, Z.; Ohsuna, T.; Sakamoto, K.; Terasaki, O.; Tatsumi, T. *Nature* **2004**, *429*, 281.
(79) Stöber, W.; Fink, A. *J. Colloid Interface Sci.* **1968**, *26*, 62.
(80) Yokoi, T.; Sakamoto, Y.; Terasaki, O.; Kubota, Y.; Okubo, T.; Tatsumi, T. *J. Am. Chem. Soc.* **2006**, *128*, 13664.
(81) Yokoi, T.; Wakabayashi, J.; Otsuka, Y.; Fan, W.; Iwama, M.; Watanabe, R.; Aramaki, K.; Shimojima, A.; Tatsumi, T.; Okubo, T. *Chem. Mater.* **2009**, *21*, 3719.
(82) Watanabe, R.; Yokoi, T.; Kobayashi, E.; Otsuka, Y.; Shimojima, A.; Okubo, T.; Tatsumi, T. *J. Colloid Interface Sci.* **2011**, *360*, 1−7.
(83) Yokoi, T.; Sakuma, J.; Maeda, K.; Domen, K.; Tatsumi, T.; Kondo, J. N. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2563−2570.