Control of Ti distribution in the zeolite framework and its impact on the catalytic properties

Toshiyuki Yokoi[1*], Xinyi Ji[1], Junko N. Kondo[1], and Hermann Gies[2]
[1]*Institute of Innovative Research, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8503 (Japan)*
[2]*Department of Mineralogy, Ruhr-Universität Bochum, 44780 (Germany)*
*yokoi@cat.res.titech.ac.jp

Introduction

With the introduction of Ti into the zeolite framework, first titanosilicate TS-1 with the MFI structure had been found and applied in various selective oxidations. Furthermore, the discovery of Ti-MWW zeolite became a milestone in both titanosilicate catalysts and heterogeneous catalysis research fields because Ti-MWW zeolite has been an active, highly selective and environmentally benign catalyst for a number of important industrially organic reactions, like the liquid-phase oxidation using H_2O_2 aq. as the oxidant [1]. The catalytic property of Ti-MWW zeolite depends on not only the Ti content but also the distribution of Ti atom. However, during the crystallization process, Ti atoms are much more difficult to incorporate with the framework compared to Al atom. As a result, the distribution of Ti atom is more complex to be evaluated and controlled in the MWW framework than that of Al atom. Herein, the influence of the preparation method for Ti-MWW on the Ti distribution was investigated. Finally, a method for controlling and estimating the Ti distribution in the zeolite framework was successfully developed

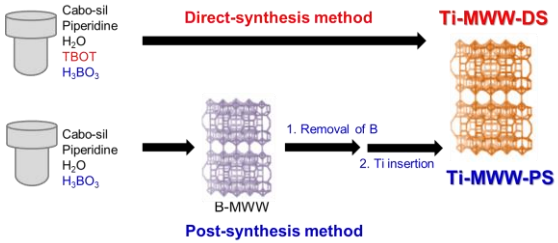

Figure 1. MWW-type titanosilicate.

Materials and Methods

Ti-MWW catalysts were synthesized by post synthesis (Ti-MWW-PS-*x*) and direct hydrothermal synthesis (Ti-MWW-DS-*x*) methods using piperidine (PI) as SDA. According to the method reported previously [2], Ti-MWW-DS-*x* was hydrothermally prepared from the mother gel with a molar ratio of 1.0 SiO_2: 0.02TiO_2: 1.4 PI: 0.67 B_2O_3: 19 H_2O under rotation (40 rpm) at 443 K for *x* hours. The obtained Ti-containing lamellar precursor was refluxed with 2 M HNO_3 aqueous solution and further calcined at 823 K for 10 h. Ti-MWW-PS-*x* catalysts were obtained by hydrothermal treatment of "silica MWW material", which was prepared by the deboronation of B-MWW, in the solution with a molar ratio of 1.0 SiO_2: 0.02 TiO_2: 1.0 PI: 19 H_2O at 443 K for *x* hours. After obtained post-synthesis Ti-containing precursor, the same acid treatment was carried out over the precursor.

Results and Discussion

For Ti-MWW-PS-*x* and Ti-MWW-DS-*x*, various characterization methods (X-ray diffraction, UV-vis, FT-IR, ICP, N_2 adsorption and desorption, NMR *et al.*) were applied to ensure the similar physical and chemical properties of these catalysts. In Table 1, the samples with Ti-MWW topology exhibited a similar Ti content, microspore volume and the BET surface area.

The comparison was first made between the samples prepared by different synthesis methods. Ti-MWW-DS-168h exhibited 8% yield of 2-MP oxidation but only around 30% yield of 1-HX oxidation. Capering with the Ti-MWW- PS-168h, the 3.4% yield of 2-MP oxidation and 56.5% yield of 1-HX oxidation were carried out. After that, the "1-HX/2-MP" index value could be calculated by the equation 1-HX/2-MP = yield for 1-HX / yield for 2-MP. Here, the 1-HX/2-MP value was defined with the ratio of the yield of oxidation 1-HX and 2-MP. Higher 1-HX/2-MP value would imply that the Ti atoms are located into narrow space like the 10-MR channels in MWW topology due to the space constraint [3, 4]. The 1-HX/2-MP value of PS-168h was larger than that of DS-168h, suggesting that Ti atoms in the Ti-MWW-PS catalyst are more located in the 10-MR channels than those in the Ti-MWW-DS catalyst. Besides, for the Ti-MWW-PS crystallized by different times, the 1-HX/2-MP value was increased from 9.4 to 16.6 by prolonging the crystallization time. This was indicated that the Ti atoms would be more embed into narrow channels than the supercages along with the crystallization time.

In conclusion, a method for controlling and estimating the Ti distribution in the MWW zeolite framework was successfully developed.

Table 1. The properties of various Ti-MWW catalysts and the yield of the oxidations of 1-hexene(1-HX) and 2-methyl-2-pentene(2-MP)

Sample-*x*	Si/Ti	PV_{micro} [a] /$cm^3\ g^{-1}$	S_{BET} [b] /$m^2\ g^{-1}$	Yield/% [c]		1-HX/2-MP [d]
				1-hexene	2-methy-2-pentene	
Ti-MWW-DS-168h	76	0.191	536	29.3	8	3.7
Ti-MWW-PS-6h	87	0.243	515	58.1	6.2	9.4
Ti-MWW-PS-48h	83	0.245	525	54.3	5.3	10.2
Ti-MWW-PS-168h	70	0.247	531	56.5	3.4	16.6

[a] PV: pore volume, micropore volume was calculated by *t*-plot method, [b] External surface area was calculated by *t*-plot method, [c] Reaction condition: Catalyst, 50mg; 1-hexane or 2-methy-2-pentene, 10mmol; H_2O_2, 10mmol; Acetonitrile, 10ml; Temp., 333 K; Time, 2h. [d] 1-HX/2-MP value : Yield for 1-HX/ Yield for 2-MP

References

1. T. Tatsumi, T. Komatsu, T. Yashima, J. Phys. Chem. B 2001, 105, 2897..
2. P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Catal. 2001,202, 245.
3. T.Yokoi, H.Nochizuki, S.Namba, J.N.Kondo, T.Tatsumi, J. Phys. Chem.C, 2015, 119, 15303-15315.
4. T. Biligetu, Y. Wang, T. Nishitoba, R. Otomo, S. Park, H. Mochizuki, J. Kondo, T. Tatsumi, T. Yokoi, J. Catal. 2017, 353, 1–10.