Synthesis and characterization of Ti-MWW with different Ti atom Distributions

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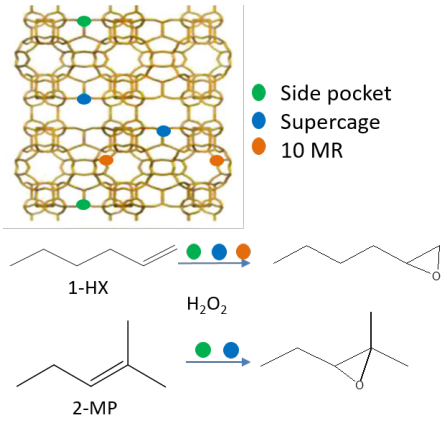
Zeolites are generally regarded as crystalline aluminosilicates connected through oxygen atoms, possessing a three-dimensional (3D) network containing channels and cavities of molecular scales. With the introduction of the transition metal titanium into the zeolite framework, first titanosilicate TS-1 with MFI structure has been found and applicated in selective oxidations [1,2]. The discovery of Ti-MWW zeolite is a milestone in both titanosilicate catalysts and heterogeneous catalysis research field because Ti-MWW zeolite is an active, highly selective and environmentally benign catalyst for a number of industrially important organic oxidation reactions, like the liquid-phase oxidation using H_2O_2 aq. as the oxidant. 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, the titanium atom is much more difficult to incorporate with the framework than the aluminum atom. As a result, the distribution of Ti atom is much more complex to be evaluated and controlled in the MWW framework than that of Al atom. Herein, a method for estimating the Ti distribution has been developed based on the selective oxidation of 1-hexene (1-HX) and 2-methyl-2-pentene (2-MP).

The catalysts had been prepared by direct synthesis (designated as Ti-MWW-DS) and post-synthesis method via boron-containing MWW precursor (designated as Ti-MWW-PS). These two kinds of catalysts possessed different Ti distributions owing to the synthesis process. The proportion of active Ti species in Ti-MWW-PS located in the 10MR channels was higher than that Ti-MWW-DS. The post synthesis, the reversible structural conversion, could make the Ti species more accessible to the narrow space like 10MR interlayer and interlayer channels.

In conclusion, a method using the catalytic property to characterize Ti distribution in zeolite framework have been developed which have been evaluated the Ti distribution in Ti-MWW zeolites.



Scheme 1 The Ti distributions in MWW framework and the reaction position

REFERENCE

[1] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Phys. Chem. B 105 (2001) 2897.
[2] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Catal. 202 (2001) 245.

Table 1 The oxidation of 1-hexane(1-HX) and 2-methyl-2-pentene(2-MP) over Ti-MWW-DS and Ti-MWW-PS

Catalyst	Si/Ti	1-HX[a]			2-MP[b]			1-HX/2-MP
		Conv.(%)	Sel.(%)	Yield(%)	Conv.(%)	Sel.(%)	Yield(%)	
Ti-MWW-PS-1	66	58.7	97.8	56.3	43.7	85.3	7.9	7.12
Ti-MWW-PS-2	116	37.5	98.3	36.9	37.1	85.8	6.3	5.86
Ti-MWW-DS	78	11.8	98.9	11.7	40.8	84.8	7.7	1.52

[a]Catalyst, 50mg; 1-hexane, 10mmol; H_2O_2, 10mmol; Acetonitrile, 10ml; Temp., 333K; Time, 2h.
[b]Catalyst, 50mg; 2-methy-2-pentene, 10mmol; H_2O_2, 10mmol; Acetonitrile, 10ml; Temp., 333K; Time, 2h.