Synthesis of TS-1 with preferably distributing Ti in depth direction of crystals and its catalytic performance

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Due to high performance as catalyst in oxidation with H_2O_2, much attention has been paid to titanium silicalite-1 (TS-1), an MFI-type titanosilicate [1]. Catalysis of TS-1 often suffers from undesirable decomposition of H_2O_2 during reaction. One of the reasons is probably that H_2O_2 is accessible to the active site in the micropore easier than bulky substrates. Improvement of H_2O_2 efficiency is a critical issue in TS-1 as oxidation catalyst. Our approach was to prepare TS-1 on which Ti species predominantly distributed in the vicinity of surface to facilitate accessibility of substrates and to inhibit H_2O_2 decomposition.

In this study, we prepared TS-1 using silicalite-1 as Si source and incorporating Ti source into the zeolite during the desilication-recrystallization process of MFI-type zeolite with tetrapropylammonium hydroxide (TPAOH) [2]. Table 1 lists the OH^- concentration in the synthesis gel to control desilication of slicalite-1.

Table1. Gel composition of synthesized TS-1

Catalyst	silicalite-1 / -	TBOT / -	TPAOH / -	H_2O / -	$[OH^-]$ / mol L^{-1}
TS-1_0.5	1.0	0.0167	0.50	33	0.70
TS-1_0.3	1.0	0.0167	0.30	33	0.44
TS-1_0.1	1.0	0.0167	0.10	33	0.16

Sample preparation was hydrothermally performed at 448 K for 1-48 h. After the crystallization, as-synthesized product was washed and dried. It was then calcined in air at 783 K for 10 h.

Fig. 1 shows typical SEM images of synthesized silicalite-1 and TS-1. After 1 h crystallization, different desilication behavior were observed for TS-1_0.5 and TS-1_0.1. Furthermore, after 48 h of crystallization, we observe that both TS-1_0.5 and TS-1_0.1 recrystallized and gave almost the same morphology as that of parent silicalite-1. We studied depth profiles of Ti species. Surface Si/Ti ratio of TS-1 after 48 h of crystallization was evaluated by XPS measurements with different argon ion etching periods (Fig. 2). As for TS-1_0.1, Si/Ti ratio increased with prolonged etching (1.78 nm/ min), suggesting that TS-1_0.1 had Ti distribution in depth direction of zeolite crystals.

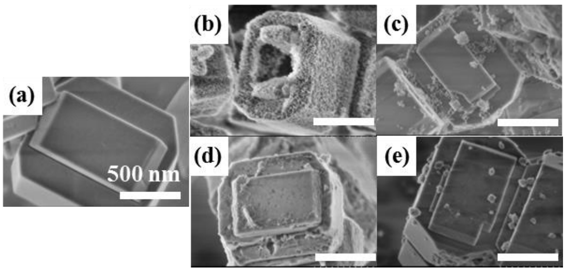

Fig. 1 SEM images of (a) silicalite-1, (b), (c) TS-1_0.5_1h, 48h and (d), (e) TS-1_0.1_1h, 48h, respectively.

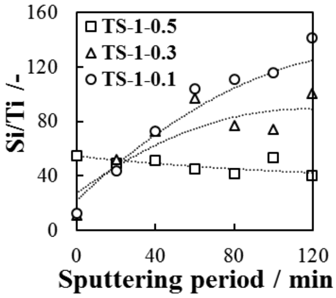

Fig. 2 Si/Ti ratio measured by XPS after argon ion etching.

Table 2 gives the catalytic properties for 1-hexene epoxidation over TS-1. TS-1_0.1 on which Ti mainly distributed in the vicinity of surface showed a higher product yield and H_2O_2 efficiency probably due to improvement of accessibility of substrates to active Ti sites.

Table 2. Catalytic activity data in 1-hexene epoxidation over TS-1

Catalyst	Si/Ti ratio / -	1,2-epoxyhexane Yield / %	H_2O_2 Conv. / %	H_2O_2 Effi. / %
TS-1_0.5	58.6	9.2	92.7	8.1
TS-1_0.3	58.0	10.5	46.2	18.8
TS-1_0.1	59.6	14.2	34.9	33.9

REFERENCES

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[2] K. Takaishi, T. Yamamoto and M. Matsukata, Chem. Lett., 45 (2016) 532-534.