Synthesis and Unique Catalytic Performance of Single-site Titanium-containing Silica with 3D Hierarchical Macroporous and Mesoporous Structure

Takashi Kamegawa*, Norihiko Suzuki, and Hiromi Yamashita
Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
*kamegawa@mat.eng.osaka-u.ac.jp

Introduction

Recently, the porous siliceous materials have attracted considerable attention because of their fascinating characteristics such as unique pore structure, unusual surface topology, and large surface area. These materials have often utilized as a support of catalytic active species such as metal nanoparticles as well as organometallic complexes. The incorporation of transition metal oxides, i.e. Ti-, Cr-, V-, Mo-oxides, within their matrixes is also one way to the design of unique catalysts. Tetrahedrally coordinated transition metal oxides exhibited unique catalytic and photocatalytic activities [1]. Among them, highly dispersed and isolated Ti-oxide moieties (single-site Ti-oxide moieties) showed remarkable catalytic properties for production of fine chemicals via selective oxidation reactions.

On the other hand, three-dimensionally (3D) ordered macroporous materials, which typically have submicrometer ranges of pores, were also intensively investigated and often designed by using close-packed uniform microspheres such as polystyrene and poly(methyl methacrylate) (PMMA). These structured materials are expected to show unique characteristics based on their size, shape, orientation and alignment [2,3].

In the present study, we dealt with the preparation of single-site Ti-containing porous silica with 3D hierarchical macroporous and mesoporous structures (Ti-MMS) and investigations on their catalytic activities in the epoxidation of linear α-olefins with different alkyl chain lengths.

Experimental

Ti-MMS was prepared by using PMMA microspheres (diameter: ca. 400 nm) as template of macropores and a precursor solution for synthesis of single-site Ti-containing mesoporous silica (Ti-MS) [3]. The structure of samples was characterized by XRD, SEM, TEM, USAXS and N_2 adsorption-desorption measurements. The local structure of Ti-oxide moieties was also confirmed by UV-vis, XAFS and photoluminescence investigations. The catalytic performances of samples were tested by the epoxidation of linear α-olefins (1-octene, 1-dodecene, 1-hexadecene, and 1-eicosene) with *tert*-butylhydroperoxide (TBHP) as oxidant.

Results/Discussion

Figure 1 shows the schematic diagram of Ti-MMS prepared by PMMA microspheres as template. Ti-MMS have 3D hierarchical macroporous structure with interconnecting networks. Single-site Ti-oxide moieties exist in the wall of macropores constructed by mesoporous silica. The formation of this unique structure was clearly confirmed by SEM and TEM investigations (Fig. 2), which was quite different as compared to Ti-MS. Ti-MS has dense powder form with an ill-defined morphology. Reflecting the structure of aligned PMMA microspheres, macroporous structure was uniformly formed in Ti-MMS. The formation of mesoporous structure was also confirmed by XRD measurements. The sharp XRD peak was observed in the region of $2\theta < 5°$. The BET surface area of Ti-MMS and Ti-MS was measured to be 1053 and 972 m^2/g, respectively. XAFS investigations also showed the successful incorporation of isolated tetrahedral Ti-oxide moieties, i.e. single-site Ti-oxide moieties, without the formation of aggregated Ti-oxides.

The comparative study using Ti-MS and Ti-MMS revealed that Ti-MMS showed higher catalytic activities for epoxidation of α-olefins compared with that on Ti-MS, especially epoxidation of α-olefin with long alkyl chain. The reaction rate was significantly enhanced on Ti-MMS depending on the increases of alkyl chain length of linear α-olefins. These results presumably accomplished by construction of 3D hierarchical macroporous and mesoporous structure leading to the decreasing the diffusion limitation and facilitating the efficient transportation of bulky reactants to the catalytically active site. The detailed characterizations and the catalytic performances of these materials will be presented.

Figure 1. The schematic diagram of Ti-MMS.

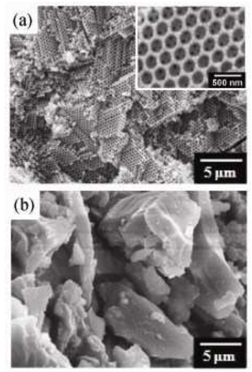

Figure 2. SEM images of (a) Ti-MMS and (b) Ti-MS.

References.

1. H. Yamashita and K. Mori, *Chem. Lett. (Highlight review)*, **36**, 348 (2007)
2. T. Kamegawa, N. Suzuki and H. Yamashita, *Energy Environ. Sci.*, in press (2011) DOI: 10.1039/c0ee00389a
3. T. Kamegawa, N. Suzuki, M. Che and H. Yamashita, *Langmuir*, in press (2011) DOI: 10.1021/la1048634