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# Synthesis and characterization of hierarchical titanium-containing mesoporous materials with MFI crystalline structure using the gas phase recrystallization for the improvement of olefins epoxidation activity

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ABSTRACT

Here we propose the synthesis of hierarchically titanium-containing mesoporous materials with MFI crystalline structure through the effective and fast post recrystallization method. The post recrystallization method consists of two steps. The first step was the easy impregnation of the structure directing agent of MFI crystalline structure on calcined mesoporous materials. The second step was the fast steam assisted conversion (SAC) process. The mother supports (Ti-MCM-41 and Ti-SBA-15) are prepared using the modified hydrothermal synthesis method, and the SAC process is conducted using the fully dried tetrapropylammonium hydroxide impregnated mother supports under an autogenous steam pressure condition in an autoclave. The prepared materials are investigated using various characterization methods. The recrystallized mesoporous materials exhibit the MFI crystalline structure both in the pore as well as on the surface, and the Ti and Si species are rearranged on an atomic level. The mesoporosity is maintained depending on the SAC process time. The influences of the recrystallization are investigated using the olefins epoxidation. The recrystallization induces the increase of more active titanium species and the surface become more hydrophobic. These influences clearly reveal the improvements in the catalytic activity. The recrystallized mesoporous materials exhibit higher catalytic activity. The conversion and selectivity are improved and the side reactions are decreased significantly.

## 1. Introduction

Since the discovery of titanium-substituted silicalite-1 (TS-1) [1], it has been investigated by many research groups, due to its ability to be applied to environmentally friendly chemical processes for the catalytic oxidation of a variety of organic chemicals [2]. Notably, the advantage of TS-1 is the development of highly efficient catalysts for the oxidation of various organic molecules with hydrogen peroxide [3–10]. This unique catalytic activity results from the isolated tetrahedrally coordinated titanium species in the framework [11,12], the hydrophobic character of the surface [6,7,13,14], and the MFI crystalline framework, which has specific architectures for active titanium centers [11,12]. However, the pore size of TS-1 limits its applications to small molecules, because TS-1 is a ten-membered ring zeolite. In order to overcome this diffusion limitation, the development of titanium-containing mesoporous materials has been reported. However, most of the developed mesoporous catalysts have fatal weaknesses as catalysts, i.e. low hydrothermal stability and hydrophilic surface nature, which originates from their amorphous (non-crystalline) structures [15–17]. Various techniques, such as silylation and the exchange of synthesis method have been proposed in order to solve this problem; however, many of these techniques are not sufficient to overcome this weakness [18–22]. Therefore, TS-1 may not be considered as a titanium-containing mesoporous catalyst except in chemical reactions with large molecules.

The development of hierarchically structured TS-1 catalysts has been reported, and these materials can possess the advantages of both the crystalline structure of zeolites and the large pore opening

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of mesoporous materials. The hierarchically mesoporous TS-1 was synthesized using carbon black, and the prepared catalyst consisted of nanosized TS-1 particles [23]. The catalytic activity of this hierarchical mesoporous TS-1 was similar to that of the conventional TS-1 and the epoxidation of large molecules (cyclohexene) was improved. A different synthesis method was introduced using the premade TS-1 seed and silanized agent [24]. These catalysts also had a nanosized TS-1 crystal structure and mesoporosity; moreover, the liquid phase epoxidation of olefin exhibited high efficiency [24]. Other researchers proposed a new synthesis method in which mesoporous TS-1 was prepared with organosilane (including long chain alkanes) by using a hydrothermal process [25]. The catalytic activity of this material with large molecules was higher than that of TS-1. In the third synthesis scheme, the mesoporous TS-1 was synthesized using as-synthesized titanium-incorporated mesoporous materials, which have a surfactant for the generation of mesoporous structure, and TPAOH (tetrapropylammonium hydroxide) as the template for the TS-1 crystalline structure. The recrystallization was induced using two types of post-treatment methods. One is based on the conventional hydrothermal synthesis process and the other is based on the DGC (Dry Gel Conversion) process [26–30]. The hydrothermal synthesis process was performed in aqueous solution in a manner similar to conventional zeolite synthesis. On the other hand, DGC process is a method of recrystallization dry gel in the gas phase and is divided into two types [31]. One of them is VPT (Vapor Phase Transformation) process is a method for including the recrystallization of the vapor of the zeolite template. The other is the SAC (Steam Assisted Conversion) process. The SAC process utilizes water vapor to induce recrystallization of dry gel containing zeolite template. The Ti-containing catalysts synthesized by above various methods also exhibited higher catalytic activity than that of TS-1 in the epoxidation of large molecules. Except for the above methods, a large number of synthesis methods have been reported and many types of mesoporous TS-1 catalysts have been prepared [32–36].

This study reports a unique and novel post recrystallization process for the simultaneous synthesis hierarchal titanium-containing mesoporous catalysts with MFI crystalline structure. The titanium-containing mesoporous materials as mother supports were prepared using a modified synthesis method [37,38]. The synthesized mother supports have thicker pore walls and long range ordered hexagonal mesoporous structures. The titanium-containing hierarchical catalysts were synthesized using a SAC method with the TPAOH impregnated mesoporous materials. The characterization of the synthesized materials was carried out using x-ray powder diffraction (XRD), small-angle x-ray scattering (SAXS), nitrogen physisorption, ultraviolet-visible spectroscopy (UV-vis), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The catalytic activity was compared with two prove reactions: small molecule epoxidation with 1-hexene and large molecule epoxidation with cyclohexene. For observation of the surface nature, epoxidation was conducted using $H_2O_2$ as the oxidant.

## 2. Experimental

### 2.1. Synthesis of mesoporous materials: Ti-MCM-41 and Ti-SBA-15

The Ti-MCM-41 was prepared using the hydrothermal restructuring method at 373 K [37]. The template solution was prepared with alkali-free deionized water, tetramethylammonium hydroxide (TMAOH) solution (10 wt% solution in water), and cetyltrimethylammonium bromide (CTMABr) at 303 K in an isothermal water bath. When the template solution became clear, the solution was cooled to room temperature. The mixture of inorganic sources was premixed with tetraethyl orthosilicate (TEOS) and titanium butoxide (TBOT) in a glove box. The prepared inorganic source was added dropwise to the template solution under vigorous stirring The molar composition of the resultant gel was TEOS: 0.02 TBOT: 0.2 CTMABr: 0.7 TMAOH: 60 $H_2O$. The obtained gel was stirred at room temperature for 1 h. The final gel was transferred to an autoclave reactor and heated without stirring at 373 K for 24 h. Then, the reactor was cooled to room temperature and the pH of the mixture was adjusted to approximately 8 using an HCl solution (2 M solution of deionized water) under vigorous stirring for more than 1 h. The resultant mixture was a white solution. After stirring for 1 h, the pH of the mixture was adjusted to approximately 10 using a TMAOH solution under vigorous stirring. This mixture was heated again at 373 K for 24 h. The pH adjustment and subsequent heating were repeated three times. Finally, the solid product was hot-filtered, washed, and dried in an oven at 373 K for 24 h. The product was calcined in air at 823 K for 5 h using a muffle furnace.

The Ti-SBA-15 was synthesized using a modified hydrothermal synthesis process [38]. The template solution of Ti-SBA-15 was prepared through combining an aqueous HCl solution (1.6 M in deionized water) with poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Pluronic P123: $EO_{20}PO_{70}EO_{20}$). The template solution was stirred until a homogenous solution was obtained, and then TEOS was slowly added to the template solution under vigorous stirring. The resulting mixture was stirred for 30 min until it became a homogeneous clear solution. At this time, 10 wt% of TBOT solution, which was premixed with isopropyl alcohol, was added under vigorous stirring and the amount of titanium was adjusted using the same molar ratio of Ti-MCM-41 ($Si/Ti = 50$). Ti-SBA-15 was prepared using a gel composition of TEOS: 0.02 TBOT: 0.017 P123: 197.2 $H_2O$: 6.1 HCl. The hydrothermal synthesis process was conducted in two steps at different temperatures. The first step was performed at 308 K for 24 h; the second step was conducted at 358 K for 24 h. All the processes were carried out in a mechanically stirred jacketed reactor equipped with a condenser and thermometer under atmospheric pressure. The stirring speed was maintained constant at 300 rpm using a speed regulator. The synthesized material was obtained via filtration and was air-dried at 373 K for 24 h. The as-synthesized Ti-SBA-15 was calcined in air at 823 K for 5 h using a muffle furnace.

### 2.2. Synthesis of mesoporous materials with MFI crystalline structure

The post recrystallization process consists of a simple impregnation process and a fast SAC process. The impregnation process was conducted using calcined titanium mesoporous materials (Ti-MCM-41 and Ti-SBA-15) as mother supports and a TPAOH solution, which was prepared with TPAOH and ethanol. The calcined Ti-MCM-41 and Ti-SBA-15 were dispersed in the TPAOH solution under vigorous stirring for 4 h. The ratio of TPAOH/mesoporous materials was fixed at 25 wt% [39]. After the dispersion of Ti-MCM-41 and Ti-SBA-15 in the TPAOH solution, they were dried using rotary evaporation at 310 K. The obtained solid products were dried in a convection oven at 373 K for 24 h.

The SAC process was performed in a Teflon-lined autoclave specifically designed for this study, which was necessary in order to avoid contact between the solid and the liquid water. The TPAOH-impregnated Ti-MCM-41 and Ti-SBA-15 were loaded into the sample holder at the center of the autoclave, and deionized water was placed on the autoclave floor. The total vacant space volume of the autoclave was measured with water, and the amount of steam in the autoclave was calculated using a steam table. The SAC process