Available online at www.sciencedirect.com

ScienceDirect

Journal of Catalysis 243 (2006) 183–191

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Synthesis and catalytic properties of a new titanosilicate molecular sieve with the structure analogous to MWW-type lamellar precursor

Weibin Fan [a], Peng Wu [b], Seitaro Namba [c], Takashi Tatsumi [a,*]

[a] *Catalytic Chemistry Division, Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama 226-8503, Japan*
[b] *Shanghai Key Laboratory of Green Chemistry and Chemical Process, East China Normal University, North Zhongshan Road 3663, Shanghai 200062, People's Republic of China*
[c] *Department of Materials, Teikyo University of Science and Technology, Uenohara-machi, Yamanashi 409-0193, Japan*

Received 31 May 2006; revised 6 July 2006; accepted 9 July 2006

Abstract

A new titanosilicate molecular sieve structurally analogous to MWW-type lamellar precursors (designated as Ti-YNU-1) was postsynthesized by adjusting the titanium content in the synthesis gel and washing the as-synthesized material with acid under refluxing conditions. The samples were characterized with XRD, ICP, TG/DTA, FTIR, UV–vis, and ^{29}Si MAS NMR techniques as well as N_2, Ar, and H_2O adsorption experiments. It was indicated that compared with Ti-MWW, Ti-YUN-1 had more silanols in the structure and that its interlayer spacing was expanded by nearly 2.5 Å. In addition, the local environment of T_1 sites of the proposed structure of Ti-YNU-1 was also different from that of Ti-MWW. This led to a great increase in the pore openings connected to supercages. The formation of Ti-YNU-1 was highly dependent on the Si/Ti ratio in the synthesis gel and also might be related to the removal of about 80% templating molecules by acid treatment before calcination. Extensive evaluation of the catalytic performance of various titanosilicates for the oxidation of different cycloalkenes showed that Ti-YNU-1 behaved like a 12-membered ring (MR) zeolite. This is further confirmed by the results that a strong peak around 6.7 Å was present in the pore size distribution curve obtained from Ar adsorption for the Ti-YNU-1 sample but absent in that for the Ti-MWW sample, and that cyclohexene conversion increased but 1-hexene conversion decreased with increasing Si/Ti ratio. Compared with the other titanosilicate materials, Ti-YNU-1 showed high activity, selectivity, and stability in the liquid-phase epoxidation of bulky cycloalkenes with H_2O_2 as an oxidant. An investigation of the effect of several protic and aprotic solvents on the catalytic property of Ti-YNU-1 in the epoxidation of cyclohexene revealed that acetonitrile should be the solvent of choice considering both conversion and selectivity.

Keywords: Cycloalkene; MWW; Oxidation; Titanosilicate, YNU-1

1. Introduction

It is well known that titanosilicate catalysts exhibit high activity and selectivity in the production of oxygenated derivatives through the oxidation of hydrocarbons, alcohols, and ketones with H_2O_2 [1–7]. In particular, the MFI-type titanosilicate, TS-1, is a very efficient catalyst in the ammoximation of cyclohexanone, the liquid-phase epoxidation of propylene, and the hydroxylation of phenol to hydroquinone and catechol under mild conditions [1,3–5]. The high reactivity of the oxirane ring makes epoxides industrially important organic intermediates for producing polyurethanes, surfactants, epoxy adhesives, and corrosion-protecting agents, additives, and so on [8]. However, TS-1 is able to catalyze the oxidation only of linear alkene and smaller cycloalkene molecules, because of its limited pore openings. In contrast, large-pore Ti-Beta can serve as a catalyst in the oxidation of bulky cycloalkene molecules [7], but the rather strong hydrophilicity and the presence of Brönsted acid sites associated with framework aluminum and/or a high concentration of silanol groups at defect sites make the activity and selectivity unsatisfactorily high [9,10]. Corma et al. recently made an attempt to delaminate MWW-type materials into isolated crystalline sheets (ITQ-2) by an elaborate method [11]; then, by grafting titanocene onto the surface of ITQ-2, they prepared the titanosilicate analogue. However, the so-prepared

---

[*] Corresponding author. Fax: +81 924 5282.
E-mail address: ttatsumi@cat.res.titech.ac.jp (T. Tatsumi).

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.07.003

material (Ti/ITQ-2) can be used with organic hydroperoxides as oxidants only under harsh conditions (i.e., in the water-free system) [12]. This is probably due to the presence of numerous hydrophilic silanols created by delamination on the exterior surface. Therefore, it is imperative to synthesize a new titanosilicate molecular sieve that not only has a larger-pore window, but also shows higher intrinsic activity and epoxide selectivity in the oxidation of bulky substrates by H_2O_2.

As we already know, MWW-type zeolite has a unique structure that contains two independent pore systems accessible via 10-MR windows. One of these systems is defined by a two-dimensional sinusoidal channel, and the other comprises supercages of 7.1 × 7.1 × 18.2 Å [13]. This may provide potential opportunities for a wide variety of applications in petrochemical and fine chemical industries. Indeed, the aluminosilicate material MCM-22 is a highly selective industrialized catalyst for benzene alkylation [14], whereas the titanosilicate analogue (Ti-MWW) is not only more active than TS-1 and Ti-Beta in the liquid-phase epoxidation of linear alkenes with H_2O_2, but also highly selective for the formation of epoxides [15]. In addition, this material also shows a unique feature of selective epoxidation of the *trans*-isomer in the oxidation of *cis*- and *trans*-2-hexenes [16]. However, for the oxidation of bulky cycloalkenes, such as cyclohexene, Ti-MWW is still inferior to Ti-Beta due to the serious steric limitation imposed by its distorted 10-MR openings [7,15]. Actually, a potential advantage to the MWW structure is expected from its interlayer supercages and side pockets, which could be very useful for catalyzing the reactions involving bulky molecules. The retention of lamellar-like structure with expanded layer spacing after calcination would be an alternative way to create the open reaction space. Such a material would make the active sites within the supercages more accessible to bulky molecules. In addition, this method would also overcome the difficulties in the delamination process; the crystalline sheet structure is inevitably partially destructed, consequently affecting the catalytic performance. Hence this method would open new possibilities for applying titanosilicates in the petrochemical and fine chemical industries. In this paper, we report the preparation, characterization, and catalytic properties of such a material in the oxidation of bulky cycloalkenes.

2. Experimental

2.1. Synthesis of samples

The samples were prepared according to the postsynthesis method [17]. First, B-MWW was synthesized from fume silica, boric acid, piperidine (PI), and distilled water with a composition of SiO_2:B_2O_3:1.4PI:19H_2O. The as-prepared solid was deboronated by calcination and reflux-washing with 6 M HNO_3 aqueous solution. The highly deboronated sample was then used as a silica source to synthesize Ti-MWW lamellar precursors with the mixture comprising SiO_2:(0–0.05)TiO_2:1.4PI:(3–20)H_2O. The resultant gel was hydrothermally treated at 170 °C for 5 days under rotating conditions. Finally, the solid product was filtered, washed, dried, further treated with 2 M HNO_3, and finally calcined at 550 °C for 10 h.

2.2. Characterization of samples

The X-ray diffraction (XRD) patterns were recorded on a MAC Science M3X 1030 X-ray diffractometer with Cu$K\alpha$ radiation (40 kV, 20 mA) to identify the crystalline phase and estimate the crystallinity. The titanium coordination states of the as-synthesized and calcined materials were investigated by diffuse reflectance (DR) UV–vis spectroscopy (JASCO V-550 UV–vis spectrophotometer). Framework and OH-region infrared (IR) spectra were measured on a PE-1600 FTIR spectrometer. Before recording the spectra in the OH stretching vibration region, the samples were first evacuated at 500 °C for 2 h under high-vacuum conditions. ^{29}Si MAS NMR measurements were performed on a JEOL JNMECA 400 nuclear magnetic resonance spectrometer at ambient temperature. The chemical shift was referenced to an external standard of polydimethylsilane. The spinning rate of the rotor was 5.0 KHz. A pulse length of 7 µs and the corresponding angle of 90° were applied, and about 3000 scans were accumulated with a repetition time of 30 s. The spectra were deconvolved with the Gaussian–Lorentzian mixed equation. N_2 adsorption at −196 °C and H_2O adsorption at 25 °C were carried out on Belsorp 28SCA and Belsorp 18SCA instruments, respectively, and Ar adsorption at −186 °C was performed on a Quantachrome Autosorb-1 instrument. Before measurement, the sample was first pretreated at 300 °C for 2 h under high-vacuum conditions. TG/DTA was measured on an ULVAC-Riko TGD 9600 thermal analysis system. The temperature was ramped to 1000 °C at a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$. The chemical composition of the samples was determined by inductively coupled plasma–atomic emission spectrometry (Shimadzu ICPS-8000E).

2.3. Catalytic measurements

The liquid-phase oxidation of alkenes with H_2O_2 (31% in aqueous solution) was carried out at 60 °C for 2 h in a round-bottom flask equipped with a condenser under stirring conditions. The temperature was controlled with a water bath. Unless specified otherwise, the reaction mixture was as follows: 0.05 g of catalyst, 10 ml of acetonitrile as solvent, 10 mmol of alkene as substrate, and 10 mmol of H_2O_2 as oxidant. The product was analyzed on a Shimadzu GC-14B gas chromatograph equipped with a 50-m OV-1 capillary column and a flame ionization detector. The amount of the unconverted H_2O_2 was determined by titrating with 0.1 M $Ce(SO_4)_2$ aqueous solution.

3. Results and discussion

3.1. Synthesis and characterization of Ti-YNU-1

XRD measurements showed that, using the postsynthesis method and washing the as-synthesized Ti-MWW lamellar precursor with acid under reflux conditions before calcination, the expanded layer structure was retained even after calcination [18]. This prepared material has been denoted Ti-YNU-1. The reason for formation of the expanded layer structure remains unclear, although we found that this formation was