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Selective liquid-phase oxidation of cyclopentene over MWW type titanosilicate

Peng Wu [a,*], Duangamol Nuntasri [b], Yueming Liu [a], Haihong Wu [a], Yongwen Jiang [a],
Weibin Fan [c], Mingyuan He [a], Takashi Tatsumi [c]

[a] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, PR China*
[b] *Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[c] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuda-chu, Midori-ku, Yokohama 226-8503, Japan*

Abstract

The epoxidation of cyclopentene has been carried out over titanosilicate catalysts of Ti-Beta, TS-1 and Ti-MWW. Ti-MWW exhibited the highest cyclopentene conversion and epoxide selectivity with either H_2O_2 or *tert*-butyl hydroperoxide as an oxidizing agent. The cyclopentene conversion depended greatly on the post treatment conditions. Acid-treated but uncalcined Ti-MWW gave cyclopentene conversion twice as high as the calcined one, while the epoxide selectivity was maintained at high levels in both cases. Various techniques such as XRD, UV–vis, ^{29}Si MAS NMR, N_2 adsorption and liquid-phase adsorption, and chemical analyses have verified consistently that the acid treatment removed the organic species located between the layers of MWW sheets, which made the interlayer entrance open and easily accessible to bulky molecules. Nevertheless, a further calcination led to a complete interlayer dehydroxyaltion and made the catalyst to be more effective for the epoxidation of linear alkenes but less active for the epoxidation of cyclic ones.

Keywords: Ti-MWW; Cyclopentene; Hydrogen peroxide; Liquid-phase epoxidation; Post modification

1. Introduction

Selective oxidations are among the most important reactions in the chemical industry. Particular efforts are being made to develop sustainable heterogeneous catalytic processes to replace those homogeneous and stoichiometrical reactions suffering serious environmental problems. The application of hydrogen peroxide to the oxidation of various organic chemicals has attracted much attention in recent years from the viewpoint of environmental and economical benefits, since it gives rise to an only byproduct of water and is less expensive and more available than the other oxidants such as peracids and organic hydroperoxides.

Over the last two decades, intensive researches have verified that the catalytic system of H_2O_2/Ti-containing zeolite is highly active and selective for the liquid-phase oxidations. MFI-type titanosilicate, TS-1, has been the most active catalyst for the oxidation of small substrates [1]. However, its medium-sized pores of 10-membered ring (MR) limit the application to the oxidations of the substrates and oxidants with relatively small molecular sizes. To overcome the disadvantages of TS-1, other titanosilicates with larger pore dimensions such as Ti-Beta, Ti-MOR, Ti-ITQ-7 and Ti-containing mesoporous materials have been developed by various methods [2–5]. Ti-Beta of 12-MR pores shows a remarkable activity for the epoxidation of cyclic alkenes but a low epoxide selectivity as a result of the solvolysis contributed by a high concentration of silanol groups on the lattice defect sites [2]. Ti-MOR has been shown to be active in the hydroxylation of bulky aromatics with H_2O_2 but not effective in the oxidation of alkenes. On the other hand, Ti-containing mesoporous molecular sieves generally are facing the distinct disadvantages of low hydrothermal stability, low intrinsic activity and easy leaching of Ti species due to their amorphous pore walls and high hydrophilicity derived from abundant surface silanol groups. More effective titanosilicates are thus urgent to be developed especially for the oxidation of bulky molecules in this field.

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* Corresponding author. Tel.: +86 21 62232292; fax: +86 21 62232292.
E-mail address: pwu@chem.ecnu.edu.cn (P. Wu).

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We have succeeded in synthesizing a novel titanosilicate with the MWW topology (typically known as MCM-22) with boric acid as a crystallization-supporting agent [6]. The three-dimensional (3D) MWW structure, formed from a lamellar precursor as a result of dehydroxylation between the layered sheets upon calcination, is expected to supply suitable spaces for incorporating highly stable and accessible Ti species and then for selective oxidations. The supercages embedded interlayers and the 12-MR side cups penetrating into the crystals from the external surface have already been demonstrated to serve as open reaction spaces in the disproportionation of toluene [7] and in the alkylation of benzene [8] in the case of MWW aluminosilicate. Owing to these unique structural properties, Ti-MWW proves to be active and selective in the epoxidation both linear and cyclic alkenes [9]; exhibits an extremely high *trans*-stereoselectivity in the epoxidation of olefinic geometrical isomers [10]; and catalyzes effectively the functionalized alkenes such as allyl alcohol and diallyl ether [11]. Despite of the catalytic effectiveness already achieved with Ti-MWW, once the 3D MWW structure is formed, the pore windows connecting to the supercages turn to be 10-MR which makes the catalytic activity not high as expected particular for bulky molecules.

In this study, we have focused on the epoxidation of cyclopentene over the titanosilicates with different framework structures with H_2O_2 or *tert*-butyl hydroperoxide (TBHP) with the purpose to synthesize cyclopentene epoxide actively and selectively, an important chemical intermediate in pharmaceutical and fragrant industry. In particular, the effects of post treatment on the catalytic properties of Ti-MWW have been investigated. Liquid-phase adsorption experiments and active site investigation using linear and cyclic alkene substrates have revealed Ti-MWW is superior in both alkene conversion and epoxide selectivity.

2. Experimental

2.1. Preparation of catalysts

Ti-MWW was hydrothermally synthesized following the procedures reported elsewhere [6]. The preparation involves the synthesis of Ti-containing lamellar precursor (Si/Ti molar ratios of 100, 70, 50, 30, 20) with piperidine (PI) as a structure-directing agent (SDA) and using boric acid as a crystallization-supporting agent, and then the removal of extraframework Ti species by refluxing the lamellar precursor in 2.0 M HNO_3 solution for 18 h. The acid-treated sample was washed with deionized water and subsequently dried at 373 K (Ti-MWW-dry) or further calcined at 823 K (Ti-MWW-cal). Other titanosilicates for control experiments, TS-1 [12] and Al-free Ti-Beta [13] were hydrothermally synthesized as reported previously. Table 1 lists several representative Ti-MWW samples together TS-1 and Ti-Beta.

Table 1
Physicochemical properties of various titanosilicates

Number	Sample	Chemical composition			N_2 adsorption	
		Si/Ti	Si/B	Si/N[a]	A_{LANG} ($m^2 g^{-1}$)	V_P ($cm^3 g^{-1}$)
1	Ti-MWW1-dry	34	30	26	530	0.12
2	Ti-MWW1-cal	34	30	∝	659	0.15
3	Ti-MWW2-dry	66	35	22	486	0.11
4	Ti-MWW2-cal	66	35	∝	576	0.13
5	Ti-MWW3-dry	132	32	21	433	0.10
6	Ti-MWW3-cal	132	32	∝	612	0.14
7	Ti-Beta	35	–	–	621	0.14
8	TS-1	38	–	–	583	0.13

[a] Determined by CHN chemical analyses.

2.2. Characterization methods

The samples were characterized by X-ray diffraction (XRD) on a MAC Science MX-Labo diffractometer, UV–vis spectroscopy on a JASCO V-550 spectrometer, ICP elemental analysis on a Shimadzu ICPS-8000E ICP atomic emission spectrometer, N_2 adsorption on a BEL SORP 28SA instrument, CHN elemental analysis on a Perkin-Elmer 2400 series II CHNS/O analyzer, and solid-state NMR spectroscopy on a JEOL JNM-ECA 400 spectrometer. ^{29}Si MAS NMR spectra were recorded at 79.5 MHz. Chemical shifts were referenced to an external standard of polydimethylsilane. A spinning rate 5.0 kHz, recycle delay time of 30.0 s, pulse widths of 7.0 μs, and 1200–4500 scans were taken. For some samples, magnetization transfer from protons to the resonant nuclei (cross-polarization) was achieved using a single contact time of 5 ms and a repetition time of 30 s. The ^{29}Si MAS NMR spectra were deconvoluted in terms of mixed Gaussian–Lorentzian equations with a JOEL software. ^{11}B MAS NMR spectra were recorded at 128.0 MHz, by using a 1.33 μs pulse length and a 2 s repetition time. Chemical shifts are referenced to H_3BO_3 as an external standard with a chemical shift of +19.2 ppm.

The liquid-phase adsorption was carried out in a glass cell (5 mL) using 1,3,5-triisopropylbenzene (TIPB) as a solvent following the procedures given elsewhere [10,14]. In a typical run, 0.1 g of adsorbent was stirred continuously in 2 g of adsorbate solution (2 wt.% of cyclopentene in TIPB). The cell temperature was maintained at 273 K with an ice-water bath. A small portion of the liquid (about 0.1 μL) was taken periodically and analyzed with gas chromatography to determine the adsorption amount.

2.3. Catalytic reactions

The liquid-phase oxidation of alkenes with hydrogen peroxide was carried out in a pear shape flask (20 mL) fitted with a condenser and a magnetic stirrer. For a typical run, a mixture of 0.05 g of catalyst, 10 mmol of alkene, 10 mmol of H_2O_2 (31 wt.% aqueous solution) or 10 mmol of TBHP (70 wt.% aqueous solution), and 10 mL of solvent was heated and agitated vigorously at a desirable temperature. The reaction mixture was analyzed with GC (Shimadzu 14 A) equipped with a 50 m OV-1 capillary column and an FID detector. The products were identified on a gas chromatograph–mass