



Epoxidation of bulky organic molecules over pillared titanosilicates



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ABSTRACT

Layered and pillared TS-1 catalysts were prepared using surfactant $C_{18}H_{37}-N^+(CH_3)_2C_6H_{12}-N^+(CH_3)_2C_6H_{13}$ in the hydroxide form as a structure directing agent and silicon(IV) ethoxide or its mixture with titanium(IV) butoxide as a pillaring medium. The pillaring treatment significantly increases the specific surface area (BET up to $685\text{ m}^2/\text{g}$) and thus the accessibility of active centres for bulky molecules. The addition of tetrabutylorthotitanate into the pillaring mixture has a positive effect on the material performance as a catalyst of cyclooctene, norbornene and α -pinene epoxidation under mild conditions, with hydrogen peroxide as the oxidant. Optimum composition of the pillaring medium is Si/Ti ratio 20. The highest yields of cyclooctene oxide (16.9% after 4 h) and norbornene oxide (14.8% after 4.5 h) were obtained using the above-prepared catalyst at 60°C with substrate/catalyst mass ratio being 10 and substrate/ H_2O_2 ratio being 2. Selective oxidation of verbenol to verbenone was observed instead of the epoxidation with the above catalysts.

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1. Introduction

Zeolites represent a rich family of porous crystalline aluminosilicates successfully applied as catalysts, adsorbents and ion exchangers [1,2]. Originally, they are powerful acidobasic catalysts; however, incorporation of other heteroelements (e.g. titanium, boron, iron, vanadium, tin, germanium and others) into the crystalline framework opened other areas of catalysis [3]. Titanium-containing zeolites are able to catalyse various oxidation reactions, e.g., epoxidation of olefins [4], oxidation of alkanes to alcohols and ketones [5], oxidation of aromatic hydrocarbons to phenols [6], ammoxidation of cyclohexanone [7], oxidation of amines to hydroxylamines [8] and thioethers to sulfoxides [9]. Furthermore, these catalysts have strong advantages in comparison with amorphous materials and other conventional oxidation catalysts: (i) they possess a regular microenvironment around the active centres [10]; (ii) the active sites are resistant to deactivation via oligomerization of metal-oxide species [10]; (iii) the materials exhibit enhanced stability towards leaching of the metal in comparison with the amorphous materials and other conventional oxidation catalysts [10].

TS-1 (MFI topology), Ti-BEA and Ti-MWW are the most frequently studied titanosilicates [3]. The TS-1 zeolite is currently a catalyst of choice for epoxidation of C=C double bonds with

hydrogen peroxide providing low waste and being environmentally friendly [11]. Its discovery [12] represents a considerable breakthrough in the field of oxidation catalysis. Presently, the TS-1 is industrially applied by Eni in a propylenoxide process [13]. However, TS-1 has pores of 5.5 \AA in diameter. Therefore, bulky substrates like terpenes cannot easily access the active sites located mainly inside the pores. Although the epoxidation of terpenes over titanosilicates has been given a certain attention, it still remains a challenge [14–16]. The application of layered materials for catalysis offers the possibility to overcome the diffusion problems [17,18] as layered materials possess high external surface areas in comparison to conventional three-dimensional titanosilicates. Ryoo and co-workers [18] reported the preparation of specially designed TS-1 in the form of nanosheets. They are formed using surfactant-based template ($C_{18}H_{37}N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2C_6H_{13}\cdot OH_2^-$) instead of conventional tetrapropylammonium hydroxide [19]. This material has been reported to exhibit activity similar to bulk TS-1 in epoxidation of 1-hexene; however, its activity is an order of magnitude higher in epoxidation of cyclooctene [18].

Wu et al. [20] succeeded in the preparation of Ti-MWW combining a synthesis of Ti-MWW lamellar precursor (denoted as Ti-MCM-22P) in the presence of boron with acidic treatment of the material to remove extra-framework Ti species prior to calcination. Later, direct synthesis of the Ti-MWW lamellar precursor Ti-YNU-1 was reported. Ti-YNU-1 exhibited higher activity in epoxidation of C_5 – C_8 cycloalkenes at 60°C than three-dimensional Ti-MWW (3D Ti-MWW, Si/Ti = 45) and Ti-BEA (Si/Ti = 35) although it had a Si/Ti ratio as high as 240 [21], demonstrating the advantages of layered

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catalysts. Subsequently, Kim et al. prepared a Ti-MCM-36 catalyst by swelling the Ti-MCM-22P layers with a surfactant and pillaring it with mesoporous silica. This material exhibited more than three times higher TON (Ti-MCM-36: 257, TS-1: 81) than the conventional TS-1 in 1-hexene epoxidation at 45 °C [22]. Wang et al. [23] reported the preparation of interlayer-expanded Ti-MWW (Ti-IEZ-MWW), which was formed using diethoxydimethylsilane. The material expresses an order of magnitude higher TON (Ti-IEZ-MWW: 233, 3D Ti-MWW: 33) compared with 3D Ti-MWW in epoxidation of cyclohexene at 60 °C.

In this contribution, we present the synthesis, properties and catalytic performance of pillared TS-1 catalysts combining the approach of Ryoo and Kim [18,22]. Parent layered TS-1 was prepared according to the Ryoo protocol. To enhance the interlayer void volume of the layered material, the pillaring treatment was applied. Formation of either silica or a mixture of silica and titania pillars between the crystalline layers helps to keep them apart when the surfactant template is removed by calcination and to improve accessibility to the active centres. Ti-MCM-36 material is included as a material formed in the same manner but possessing a different topology of the crystalline layers. The materials are compared with conventional 3D TS-1 as catalysts in selective epoxidation with hydrogen peroxide as the oxidant. Cyclooctene, norbornene, α -pinene and verbenol are used as model substrates.

2. Experimental

2.1. Synthesis of two-dimensional TS-1

The syntheses of parent-layered TS-1 was carried out according to the reported procedure [18] from silicon(IV) ethoxide (TEOS; Aldrich 98%) and titanium(IV) butoxide (TBOTi; Aldrich 97%) using a surfactant template $C_{18}H_{37}N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2C_6H_{13}$ in the hydroxide form ($C_{18-6-6}OH_2$; prepared as described in the literature [18]). Typically, TBOTi was added drop-wise into TEOS and stirred for 30 min. Then an aqueous solution of the template was added to the mixture and homogenized at 60 °C for 3 h. Evaporated ethanol was replaced with the same mass amount of water. Synthesis mixture of composition 100 TEOS: 2.5 TBOTi: 6 $C_{18-6-6}OH_2$: 5000 H_2O was hydrothermally crystallized in a Teflon-lined autoclave at 160 °C for 236 h under agitation. After the given time, the zeolite was filtered off, washed with water, dried at 80 °C and finally calcined or subjected to the pillaring treatment. Calcination was carried out at 570 °C for 8 h, using a temperature ramp of 1 °C/min.

No swelling of the material was necessary as the layers are swollen intrinsically by the surfactant template. The pillaring was performed as per the Kim procedure [22]. TEOS or a mixture of TEOS and TBOTi in a given Si/Ti ratio was mixed with the as-synthesized dry layered zeolite (10 g of the TEOS mixture per 1 g of the zeolite) and stirred at 65 °C for 24 h. Then the mixture was centrifuged and the solid material was dried for 48 h at room temperature. Subsequently, the product was hydrolysed in water with 5% of ethanol (100 ml/1 g) at ambient temperature for 24 h under vigorous stirring. Ethanol in the mixture helps to disperse the hydrophobic titanate. Finally, the solid material was centrifuged again, dried at 65 °C and calcined in an airflow at 550 °C for 10 h using the temperature ramp of 2 °C/min.

2.2. Synthesis of Ti-MCM-36

The synthesis followed the procedure described by Tatsumi [20]. 26.1 g of piperidine (Aldrich, 99%) was added to 73.3 g of distilled water and stirred for 15 min. The solution was separated into two parts and 2.57 g of TBOTi (Si/Ti 30) was added into one part and

17.74 g of H_3BO_3 (Fluka, 99%, Si/B 0.75) was added to the other part. The solutions were stirred for about 50 min. 12.86 g of Cab-O-Sil M5 (Havel Composites, Czech Republic) was divided into two parts and each was slowly added into the solution and stirred for another 60 min. Then, both slurries were mixed together and stirred for next 60 min. The final gel was charged into Teflon-lined autoclave. The crystallization proceeded under agitation and autogenous pressure at 130 °C for first 24 h, and then the temperature was increased to 150 °C. After 24 h, the temperature was increased to 170 °C for the final 5 days. Solid product was collected by filtration, washed with distilled water and dried in the oven at 60 °C overnight. The as-synthesized Ti-MCM-22(P) was stirred at 85 °C with 2 M HNO_3 for 15 h (20 ml/1 g) to remove extra-framework Ti species.

The Ti-MCM-22(P) was swollen using 20 ml/1 g of 25% solution of cetyltrimethylammonium hydroxide ($C_{16}TMA-OH$, prepared by ion-exchange from chloride form). The slurry was stirred for 16 h at ambient temperature. The product Ti-MCM-22SW was separated by centrifugation, washed with water and dried at 60 °C.

Pillaring of Ti-MCM-22SW was carried out with TEOS (50 ml/1 g). The mixture was stirred at 85 °C for 16 h. The solid product was isolated by centrifugation and dried at ambient temperature. Subsequently, the material was hydrolysed in water (100 ml/1 g) at ambient temperature for 24 h. Finally, the product was centrifuged again, dried at 60 °C and calcined in the airflow at 550 °C for 10 h using the temperature ramp of 2 °C/min.

2.3. Synthesis of three-dimensional TS-1

Conventional titanate TS-1 (3D TS-1) was prepared from a gel with an initial Si/Ti ratio of 40 according to the procedure described in ref. [19] using tetraethyl orthotitanate (Aldrich, technical grade) and tetraethyl orthosilicate with tetrapropylammonium hydroxide (Aldrich, 20% in water) as a structure directing agent.

2.4. Characterization

X-ray powder diffraction (XRD) patterns were collected using a Bruker AXS D8 Advance diffractometer equipped with a graphite monochromator and a position-sensitive detector Vântec-1 using $Cu K\alpha$ radiation in Bragg–Brentano geometry. Data were collected in continuous mode over the 2θ range of 1–40°.

The size and shape of zeolite crystals were examined by scanning electron microscopy (SEM) on a JEOL, JSM-5500LV microscope. The images were collected with an acceleration voltage of 20 kV.

Nitrogen sorption isotherms were measured at liquid nitrogen temperature (–196 °C) with Micromeritics Gemini volumetric instrument. Prior to the sorption measurements, individual zeolites were outgassed in a stream of helium at 300 °C for 3 h.

BET area was evaluated using adsorption data in the range of a relative pressure from $p/p_0 = 0.05$ to 0.25. The t -plot method [24] was applied to determine the volume of micropores (V_{micro}) and external surface area (S_{ext}). The adsorbed amount of nitrogen at $p/p_0 = 0.95$ reflects the total adsorption capacity (V_{total}).

DR-UV/Vis absorption spectra were collected using Perkin-Elmer Lambda 950 Spectrometer with a 5 or 2 mm quartz tube and a large $8 \times 16 \text{ mm}^2$ slit. The data were collected in the wavelength range of 190–500 nm. All the samples were analysed after calcination.

Chemical composition of the materials (expressed hereafter as a Si/Ti ratio) was determined by XRF with a spectrometer Philips PW 1404 using an analytical program UniQuant. The samples were mixed with dentacryl as a binder and pressed on the surface of cellulose pellets.

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