Microporous and Mesoporous Materials 212 (2015) 48–55

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Effect of treatment with different bases on the catalytic properties of TS-1/SiO_2 extrudates in propylene epoxidation

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A R T I C L E I N F O

Article history:
Received 18 November 2014
Received in revised form
21 March 2015
Accepted 23 March 2015
Available online 28 March 2015

Keywords:
TS-1
TS-1/SiO_2
Base treatment
Propylene epoxidation

A B S T R A C T

The effect of treatment with organic bases (ethylamine (EA), tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH) and tetrapropylammonium hydroxide (TPAOH)) on the catalytic properties of TS-1/SiO_2 extrudates was investigated in the epoxidation of propylene. The morphology and MFI structure of the TS-1 were destroyed and the amount of non-framework Ti species in the catalysts increased when the TS-1/SiO_2 extrudates were treated with EA and TMAOH, due to desilication. These changes are opposite to the improvement of the catalytic properties. On the contrary, treatment with TEAOH and TPAOH made the crystalline structure of the catalysts more homogeneous and adjusted the distribution of Ti and Si in the catalysts. In addition, the acidity of the samples increased appreciably, the pore openings at the surface of the catalysts were expanded as revealed by a series of characterizations. Thus, the catalytic activity and stability of the two catalysts were substantially enhanced.

1. Introduction

Titanium silicalite molecular sieve (TS-1) with MFI topology was first hydrothermally synthesized by Taramasso et al., in 1983 [1]. Selective oxidations with dilute hydrogen peroxide as oxidant over TS-1 were studied for decades [2–5] and the hydroxylation of phenol, the ammoxidation of cyclohexanone, and the epoxidation of propylene have been commercialized. The HPPO (hydrogen-peroxide-to-propylene-oxide) process, which produces propylene oxide with dilute H_2O_2 using TS-1 as catalyst, has attracted much attention during recent years, because it is an economically and environmentally benign process [6,7]. The high catalytic activity and stability of TS-1 is one of the key factors in the HPPO process.

Numerous efforts have been made to improve the catalytic properties of TS-1 catalysts, including optimizing synthesis methods and materials [8–18]. Different Ti sources [8–11], nonionic surfactants and ammonium salts [12–14] were introduced to obtain a higher content of framework Ti and hierarchical and nanosized TS-1 was synthesized to eliminate intracrystalline diffusion limitation [15–18]. Alkali treatment, which is one of the methods for synthesizing hierarchical TS-1, was widely studied during in the past decade, due to the simple and efficient improving of the catalytic performance [19–21]. A hierarchical TS-1 with well-developed mesopores was obtained treating TS-1 with NaOH followed with HCl gradually, accompanied by the desilication of TS-1. It showed good catalytic activity for the oxidation of small molecules and a significantly higher activity for the bulky ones [22]. Xue et al. [23] found that some large hollows (50 × 70 nm and 70 × 110 nm) were formed in the TS-1 crystals, and the distribution of Ti was changed by treating TS-1 with ethanolamine. These changes led to the improvement of catalytic activity and stability for continuous ammoxidation of cyclohexane. Wang et al. [24] demonstrated that the formation of hollow structure accompanied by a reincorporation of Ti in the framework during treatment with tetrapropylammonium hydroxide (TPAOH) increased the catalytic activity. Similar observations were reported by Zuo et al. [25] and Wu et al. [26] on the effect of treatment with TPAOH. Zuo et al. also discovered that the recrystallization preferred to occur *a*-oriented when using TPAOH to modify TS-1, but *b*-oriented when using tetrabutylammonium hydroxide (TBAOH). Wu et al. found that the catalyst stability was increased after the TPAOH treatment, but the activity and the selectivity of TS-1 changed hardly.

However, these studies were made with TS-1 in powder form. For industrial application, TS-1 powder must be shaped to decrease

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http://dx.doi.org/10.1016/j.micromeso.2015.03.026
1387-1811/

the pressure drop and achieve an appropriate mechanical strength [27–29]. It was found that the micropores of the treated TS-1 powder were blocked by extrusion [28–30]. It is imperative to develop a method to directly improve the catalysts properties for industrial application. In our previous work [30], we found that the treatment of TS-1/SiO_2 extrudates is much more effective on improving the catalytic properties than that of TS-1 powder. Some differences appeared in the physicochemical properties of treated TS-1/SiO_2 extrudates and treated TS-1 powder, such as hydrophobicity, elemental distribution and particle morphology.

In this paper, we further investigated the effect of treatment with organic bases on the catalytic properties of TS-1/SiO_2 extrudates in the epoxidation of propylene. The adopted organic bases are ethylamine (EA), tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH) and tetrapropylammonium (TPAOH). The influence of treatment on the diffusion properties and elemental distribution was studied in detail. By comparing the characterization and evaluation in epoxidation of propylene, we found that different organic bases led to completely different results in the two types of TS-1.

2. Experimental

2.1. Catalyst preparation

TS-1 powder was synthesized as described in Ref. [31]. TEOS and TBOT were used as silicon and titanium sources, respectively. TPAOH was used as the template. TS-1 powder samples crystallized from gels with the following molar composition: $SiO_2 \cdot 0.026TiO_2 \cdot 0.3TPAOH \cdot 30H_2O$. The gel was transferred into an autoclave, and heated to 443 K and kept for 48 h. The crystalline products were collected by centrifugation, and washed with distilled water. After drying at 373 K, the sample was calcined at 813 K for 6 h.

TS-1/SiO_2 extrudates were prepared by mixing 30 wt. % silica sol (20.2 g), TS-1 (20.0 g), and sesbania powder (1.3 g). Then the mixture was extruded into extrudates with a diameter of 2 mm. The extrudates were cut into 1–2 mm long, dried at 393 K for 2 h and calcined at 813 K for 6 h in air.

TS-1/SiO_2 extrudates were treated with 0.06 mol/L organic base solutions, and the ratio of TS-1/SiO_2 to base solution was 1 g: 5 mL. The treatment was carried out in a Teflon-lined autoclave at 443 K for 72 h without stirring. The autoclave was then rapidly cooled and the catalysts were separated by filtration, washed with distilled water, dried at 373 K and calcined at 813 K for 6 h in air. The treated catalysts were denoted as TS-1/SiO_2-a, where a represented the base used in the treatment. For example, the sample treated with 0.06 mol/L EA solution was denoted as TS-1/SiO_2-EA. The untreated sample was denoted as TS-1/SiO_2.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) was performed on a Japan Rigaku D/MAX-2400 instrument using CuK_α radiation. UV-Vis spectra were obtained on a Jasco UV-550 spectrometer from 190 to 500 nm with $BaSO_4$ as a reference. UV Raman spectra were recorded on a DL-2 Raman spectrograph. The 244 nm line of a LEXEL laser and the 325 nm line of a He–Cd laser were used as the excitation sources. An Acton triple monochromator was used as spectrometer for Raman scattering. The spectra were collected by a Princeton CCD detector. The power of the laser line at the sample was below 5 mW. The microstructure of the samples was studied with a Tecnai G^2 F30 transmission electron microscope. The chemical compositions of the samples were determined with a Perkin–Elmer OPTIMA 2000DV ICP optical emission spectrometer (ICP-AES). Nitrogen sorption measurements were performed at liquid nitrogen temperature on a Quantachrome AUTOSORB-1 physical sorption apparatus. Total surface area and pore volume were calculated according to the BET method and HK model. X-ray photoelectron spectra (XPS) were acquired on a Thermon ESCAlab 250 spectrometer (USA) using Al $K\alpha$ radiation. Binding energies were referenced to C 1s line (285.0 eV) and determined with a precision of 0.1 eV. The XPS peak area ratios were determined by integrating areas of the Ti 2p, O 2p, and Si 2p peaks, using the XPSPEAK 4.1 program. Isothermal adsorption capacities for *n*-hexane and cyclohexane were measured on a home-made instrument by a flow gravimetric method at 298 K. The sample was dehydrated at 627 K in a quartz tube for 1 h under in a flow of 35 mL/min N_2. After dehydration, the sample was put into the isothermal chamber, and then 50 mL/min of N_2 carrier gas saturated with 5 mL/min adsorbate vapor passed through the sample until the adsorption-desorption equilibrium was achieved. The catalyst was weighed using an electronic balance. The equilibrium adsorption capacity was defined as molar amount of the adsorbate per gram of sample. Solid-state ^{29}Si magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra were performed on a Bruker 500 WB nuclear magnetic resonance spectrometer at ambient temperature. The chemical shift was referred to an external standard of tetramethylsilane (TMS). The spin rate of the rotor was set at 4.0 kHz, and a typical $\pi/4$ pulse length of 2.73 μs was adopted for ^{29}Si resonance. The spectra were deconvoluted with a Gaussian–Lorentzian mixed model. Infrared spectroscopy with pyridine (Py) adsorption (Py-IR) was carried out using an EQUINOX55 Fourier-transform infrared spectrometer (FT-IR) (Bruker Corp.) with a resolution of 4 cm^{-1}. NH_3 temperature-programmed desorption (NH_3-TPD) experiments were performed on a CHEMBET 3000 chemical absorber (Quantachrome, USA). The catalyst was pretreated in flowing He (40 mL/min) at 773 K for 1 h. After adsorption of NH_3 at 393 K, the He flow was continued for an additional 30 min to remove excess NH_3. The reactor temperature was raised to 923 K at a rate of 10 K/min.

2.3. Propylene epoxidation

The epoxidation of propylene was carried out in a stainless steel batch reactor. In a typical run, 0.15 g of catalyst, 9.1 mL of 30 wt.% of H_2O_2 and 24.9 mL of methanol were fed into the reactor. Then propylene was charged at constant pressure (0.4 MPa) and the mixture was heated at 313 K under magnetic stirring for 60 min.

The epoxidation of propylene was also carried out in a fixed-bed reactor. The amount of catalyst used in the reaction was 3.5 g and typical reaction conditions were as follows: 3.0 MPa, 313 K, H_2O_2 (50 wt.%), methanol as solvent (CH_3OH: H_2O_2: H_2O = 6.2: 1.0: 1.0, weight ratio). In detail, the weight hourly space velocity (WHSV) of propylene was set at 1.4 h^{-1}, the molar ratio of propylene to H_2O_2 was at 3.0, and 0.12 mmol/L ammonia was used to neutralize the acid centers in the reaction substrate.

The initial and residual H_2O_2 concentration was measured by iodometric titration. The products of the reaction were analyzed on a 7890F gas chromatography with a FID and PEG-20M column (30 m × 0.25 mm × 0.4 μm). PO was the main product and propylene glycol monomethyl ether (MME) and propylene glycol (PG) were byproducts. The conversion of H_2O_2 ($X(H_2O_2)$), selectivity of PO (S(PO)), and utilization of H_2O_2 ($U(H_2O_2)$) are given using the following definitions:

$$X(H_2O_2) = (n_0(H_2O_2) - n(H_2O_2))/n_0(H_2O_2) \times 100\%$$