



Short communication

The synthesis, characterization and catalytic activity of the hierarchical TS-1 with the intracrystalline voids and grooves

Baorong Wang, Min Lin ^{*}, Bin Zhu, Xinxin Peng, Guangtong Xu, Xingtian Shu

State Key Laboratory of Catalytic Material and Reaction Engineering, Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China

ARTICLE INFO

Article history:

Received 28 July 2015

Received in revised form 31 October 2015

Accepted 9 December 2015

Available online 11 December 2015

Keywords:

Hierarchical TS-1

Intracrystalline voids

Grooves

TPAOH

NaOH

ABSTRACT

Hierarchical TS-1 with grooves and intracrystalline voids was prepared by TPAOH/NaOH treatment. With increasing NaOH concentration, the dissolution–recrystallization process was intensified, the relative crystallinity and microporous properties decreased, the secondary pore volume increased. Although the dissolved species could be recrystallized, Na⁺ prevented the titanium incorporation, which increased the extra-framework titanium content. In phenol hydroxylation, improved activity and H₂O₂ efficiency were achieved when NaOH was no more than 0.1 mol/L, which may be a result of the positive influences of the secondary pores. At higher NaOH concentration (>0.1 mol/L), the activity and H₂O₂ efficiency decreased due to the negative influences of the non-framework titanium.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Titanium silicalite-1 (TS-1) with MFI topology is well-known for the excellent selective oxidation performance under mild condition [1]. With aqueous H₂O₂ as the oxidant, TS-1 has been widely used in phenol hydroxylation [2,3], epoxidation of alkenes [4,5], oxidation of alkanes [6], cyclohexanone ammoximation [7] and oxidative desulfurization [8]. Nowadays, TS-1 has been successfully industrialized in phenol hydroxylation, cyclohexanone ammoximation and propylene epoxidation [9,10].

Although TS-1 exhibits good activity in the oxidation of many organic compounds, the micropore size is about 0.55 nm. Thus, substrates with larger molecular size cannot enter the channels, and they could only interact with the active sites on the external surface. In order to enhance the accessibility of active centers, hierarchical TS-1 with well-developed secondary porosity was synthesized by desilication [11], silanization [12, 13], dissolution–recrystallization [14,15], dry gel conversion [16], soft templating [17,18] and hard templating [19]. When TS-1 was treated with aqueous NaOH, the silica framework was dissolved, and mass loss was inevitable [11]. When TS-1 was modified with tetrapropyl ammonium hydroxide (TPAOH), the erosion was mainly in the inner part of zeolite particles, and the dissolved species could be recrystallized [14,20]. Then, hierarchical TS-1 with intracrystalline voids, better catalytic activity and stability could be obtained.

When inorganic base or organic alkali was used only in the post-synthesis of hierarchical TS-1, the influences on physiochemical properties and catalytic activity were reported in many literatures. But when

inorganic base and organic alkali were simultaneously used, the influences are still unknown. Herein, we report the preparation of hierarchical TS-1 by treatment with TPAOH and NaOH, and influences of NaOH concentration on the physiochemical properties and catalytic activity were studied.

2. Experimental

2.1. Synthesis of TS-1

TS-1 was synthesized following the procedure reported by Thangaraj [21]. Tetraethyl orthosilicate (TEOS) was the silica source, tetrabutyl titanate (TBOT) was the titanium source, and TPAOH (25 wt.%) was both the structure directing agent and alkali source. TEOS was firstly hydrolyzed with TPAOH for 3 h, then TBOT dissolved in anhydrous isopropyl alcohol was dropped into the hydrolyzed solution. Finally, water was added and the mixture was stirred at 80 °C for 3 h to remove alcohol. The chemical composition of the final gel was SiO₂:TiO₂:TPAOH:H₂O = 1:0.04:0.4:40, and it was transferred to a Teflon-lined stainless-steel autoclave. The crystallization was carried out under autogenous pressure at 175 °C for 5 days. The mixture obtained was filtered, washed with distilled water, dried at 110 °C for 6 h, and calcined at 550 °C for 5 h.

2.2. Post-synthesis

Firstly, 1 g of the previous prepared TS-1 was mixed with 15 mL mixed solution of TPAOH (0.2 mol/L) and NaOH (0.05, 0.10, 0.15 and 0.20 mol/L), the mixture obtained was transferred to a Teflon-lined

* Corresponding author.

E-mail address: linmin.ripp@sinopec.com (M. Lin).

stainless-steel autoclave. The treatment was carried out under autogenous pressure at 145 °C for 4 h. Secondary, the mixture was filtered, washed with distilled water, dried at 110 °C for 6 h, and calcined at 550 °C for 5 h. Finally, the samples were magnetically stirred in aqueous HNO₃ (80 °C, 0.5 mol/L) for 6 h. Then, the samples were filtered, washed with distilled water, dried and calcined. The samples obtained were denoted as TS-1-P-xNaOH, in which x represents the NaOH concentration.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained on a Philips Panalytical X'pert diffractometer with nickel-filtered Cu K α radiation. Scanning electron microscopy (SEM) images were taken from a Hitachi 4800 microscope, transition electron microscopy (TEM) images were recorded on a JEOL JEM-2100 microscope. N₂ adsorption–desorption isotherms were collected at 77 K on a Micromeritics ASAP 2405 apparatus. The samples were previously dried under vacuum (0.1 Pa) at 573 K for 6 h, and surface parameters were derived from the isotherms using BET and t-plot methods. UV–visible (UV–Vis) spectra were recorded on a JASCO UV–visible 550 spectrometer. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo-Fischer-VG ESCALAB250 with Mg K α radiation, and the framework titanium content and non-framework titanium content were integrated results of the Ti 2p_{3/2} peaks at 460.3 and 458.7 eV.

2.4. Phenol hydroxylation

The phenol hydroxylation was carried out in a round-bottomed flask equipped with a condenser and a magnetic stirrer. Typically, 0.2 mol phenol was dissolved in 17.2 mL acetone, then 0.9 g catalyst and 6.8 g aqueous hydroperoxide (30 wt.%) were added, the molar ratio of H₂O₂ and phenol was 0.3. Under stirring, the reaction system was kept at a constant temperature of 80 °C for 0.5 h. The reaction products were analyzed by an Agilent 6890 N equipped with a FFAP capillary column. The H₂O₂ concentration was analyzed by iodometric titration.

3. Results and discussion

3.1. Physicochemical properties

Fig. 1 shows the XRD patterns of TS-1 and hierarchical TS-1, in which the crystallinity of parent TS-1 was denoted as 100%, while the relative crystallinity (RC) of hierarchical TS-1 was calculated by comparing the integrated area of the characteristic peaks between 22–26° with that of TS-1. It was clearly illustrated that the MFI topology was preserved

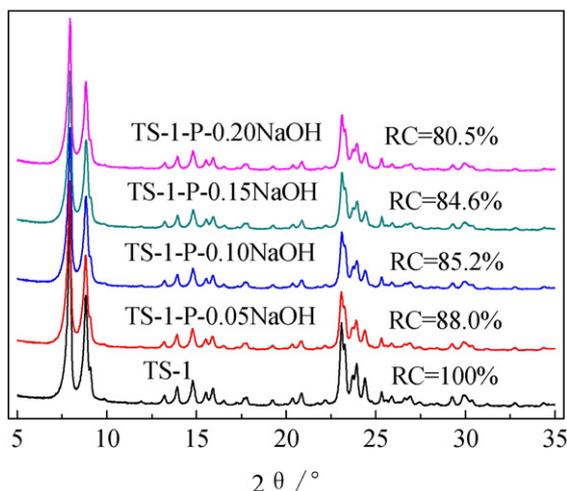


Fig. 1. XRD patterns of TS-1 and hierarchical TS-1.

after the TPAOH/NaOH treatment. However, the relative crystallinity decreased by about 12% when NaOH was 0.05 mol/L, and the decrease was more significant with higher NaOH concentration (≥ 0.10 mol/L). It has been reported that the silica species in MFI topology could be selectively dissolved in basic media [22]. When TS-1 was treated with aqueous NaOH, the crystals could be eroded [11]. However the dissolved species could be recrystallized to protect the MFI topology in presence of TPAOH [15]. In TPAOH and NaOH solution, there were dissolution and recrystallization. However the erosion effect should be more significant than the recrystallization effect, especially when the NaOH concentration was high, which was proved by the decrease of the relative crystallinity.

The N₂ adsorption desorption isotherms are collected at 77 K. Large hysteresis loops in hierarchical TS-1 were observed, indicating that mesopores with pore size larger than 4 nm were created by TPAOH/NaOH [23,24]. As the hysteresis loops suddenly closed at about P/P₀ = 0.45, the adsorption branch was preferred for pore size calculation with BJH method, and the results were shown in Fig. 2. The mesopores in TS-1-P-0.05NaOH were widely distributed in the range of 16–32 nm, and a wider distribution of the mesopores could be observed in TS-1-P-0.15NaOH and TS-1-P-0.2NaOH. Moreover, the surface parameters are illustrated in Table 1. For TS-1-P-0.05NaOH, the specific surface area (S_{BET}), microporous area (S_{MI}) and microporous volume (V_{MI}) decreased separately by 4.8%, 21.1% and 25.6%, while the external surface (S_{MA}) and secondary pore volume (V_{SP}) increased respectively by 154.8% and 127.0%. At higher NaOH concentration, the changes of the surface parameters were more significant. When NaOH was 0.20 M, the S_{BET} , S_{MI} and V_{MI} decreased respectively by 8.5%, 27.6% and 30.9%, while the S_{MA} and V_{SP} increased by 183.3% and 205.6%. Combined with the results of pore size distribution, the secondary pores were introduced at the expense of the micropores, and larger secondary pore volume could be obtained at high NaOH concentration.

Fig. 3 shows the SEM images. The parent TS-1 crystal was an aggregate of small particles, but the surface of the particles was smooth. However the surface was etched by TPAOH/NaOH, and grooves on the surface could be observed, which was different from the relative smooth surface obtained by TPAOH modification. It gave direct information of the severe erosion in TPAOH/NaOH solution. Although the TPA⁺ cations were supposed to deposit on the external surface of the zeolite particles, and protect the surface from the OH⁻ attack [25]. The faster dissolution of the framework in NaOH than in TPAOH may result in the severe etching on the surface [26], even when NaOH was 0.05 mol/L.

The TEM images are shown in Fig. 4. Accumulated pores were observed in parent TS-1, and hierarchical TS-1 with intracrystalline voids, part of which linked directly to the surface, was prepared by TPAOH/NaOH treatment. Crystals with smaller size and no intracrystalline

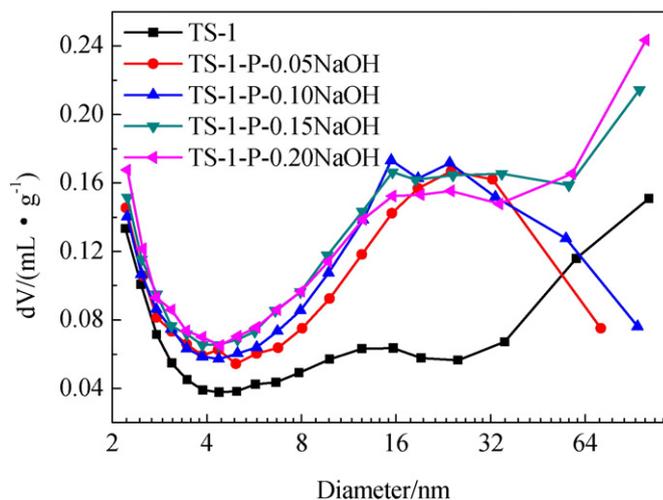


Fig. 2. Pore size distribution of TS-1 and the hierarchical TS-1.

Download English Version:

<https://daneshyari.com/en/article/49220>

Download Persian Version:

<https://daneshyari.com/article/49220>

[Daneshyari.com](https://daneshyari.com)