Microporous and Mesoporous Materials 247 (2017) 16–22

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Effects of crystal size and pore structure on catalytic performance of TS-1 in the isomerization of styrene oxide to phenyl acetaldehyde

Xiong-Fei Zhang [a], Jianfeng Yao [a, *], Xiaoxia Yang [b]

[a] College of Chemical Engineering, Nanjing Forestry University, Nanjing, 210037, PR China
[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, PR China

ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form
23 March 2017
Accepted 24 March 2017
Available online 27 March 2017

Keywords:
Hierarchical porosity
Crystal size
TS-1
Isomerization
Styrene oxide

ABSTRACT

In this study, isomerization of styrene oxide to phenyl acetaldehyde was investigated over a series of TS-1 catalysts with different crystal sizes and post-treatment methods under a gas-phase atmosphere free of solvents. The physicochemical properties of the samples were characterized by a combination of N_2 adsorption, XRD, NH_3-TPD, UV–vis, FT-IR and SEM. By the characterization of catalysts and investigation of their catalytic performances, results indicated that nano size TS-1 exhibited better anti-coking ability and phenyl acetaldehyde selectivity than micro size TS-1. Additionally, TPAOH treatment led to the development of considerable mesoporosity without significant destruction of its intrinsic zeolite properties. The results highlighted that the existence of well-developed hierarchical pore systems in TS-1-O could reduce diffusion path length and enhance transport of phenyl acetaldehyde out of the zeolite crystals, thus markedly improving catalytic stability and selectivity. However, upon NaOH treatment, the micropore structures were irreversibly destroyed accompaning with the amorphization of the zeolite crystals.

1. Introduction

Phenyl acetaldehyde is an important organic compound for the production of fragrances and polymers [1,2]. One important process for the preparation of phenyl acetaldehyde is by the isomerization of styrene oxide in the presence of acid catalysts [3–6]. The conventional homogeneous catalysts faces the problems of environmental pollution, low yield and self-condensation of products, which limits its application on industrial scale. More and more attention has been shifted to environmentally benign heterogeneous catalysts. Various solid materials have been applied as catalysts for the isomerization of styrene oxides, such as metal oxides, zeolites, natural silicates and heteropoly acid [3,7–10]. Among them, zeolites are thought to be superior to others on account of their acidity and pore structure can be adjusted by a series of synthesis and post-synthesis methods.

Especially for the MFI type zeolites, building of an intersecting micropore network composed of straight channels and zigzag channels, exhibit promising activity and selectivity. Nevertheless, the competitive aldol condensation and polymerization of aldehyde products still accelerate the deactivation of the catalysts. Prior literature [11–13] provide evidence that coke is preferentially formed on strong acid sites and the catalyst lifetimes are prolonged as the strong acid strengths decrease. In addition, Gou et al. [14] have investigated the catalytic performance of alkali-treated ZSM-5 zeolites for the isomerization of styrene oxide to phenyl acetaldehyde and found that the development of hierarchical zeolites can reduce diffusion path length and shorten the contact time between reactants and catalyst bed. Hence, a modified MFI-type zeolite with moderate acidity and pore systems may be favorable to this reaction.

Compared with ZSM-5, TS-1 exhibits less amount of strong acid sites and more weak acid sites, this material has been applied as efficient catalyst in diverse commercial applications [15–21]. Moreover, to overcome the steric and intracrystalline diffusion limitations, several approaches have been developed in the last few years including alkaline treatment [14,22–25], modification with crystal size [26] and deposition with polysiloxane [27], etc. In present work, a series of TS-1 catalysts with different crystal sizes and post-treatment methods were synthesized to improve he diffusion properties. Physicochemical properties of the samples were characterized by a combination of N_2 adsorption, XRD, NH_3-TPD, UV–vis, FT-IR, SEM and TEM. The catalytic performance was

---

* Corresponding author.
E-mail address: jfyao@njfu.edu.cn (J. Yao).

http://dx.doi.org/10.1016/j.micromeso.2017.03.047

evaluated on a fixed-bed reactor under a gas-phase atmosphere free of solvents. To the best of our knowledge, this work is the first to apply TS-1 catalysts to the synthesis of phenyl acetaldehyde.

2. Experimental

2.1. Catalyst preparation

Nano size TS-1, denoted as TS-1-nano, was synthesized hydrothermally from a gel mixture of $1SiO_2$:$0.03TiO_2$:0.3TPAOH:$30H_2O$ following the procedure reported by Sivasanker et al. [28]. In a typical synthesis, TEOS and TBOT were used as Si precursor and Ti precursor, respectively. First, the required amount of TEOS was added to a mixture of TPAOH and distilled water drop wise. Then, certain amount of TBOT was added to isopropanol under vigorous stirring for 0.5 h. The final obtained mixture was reacted at room temperature for 5 h, followed by hydrothermal aging at 80 °C for 3 days in a round-bottom flask. Crystallization was performed in a Teflon lined stainless-steel autoclave at 170 °C for 5 days. After cooling down, the solid product was filtered, washed several times, dried overnight at 105 °C and finally calcined under air condition at 550 °C for 8 h.

Micro size TS-1, denoted as TS-1-P, was obtained from JCNANO Tech Co., Ltd (Nanjing, China). Post-synthetic procedures of desilicication were adapted from the methodology proposed by Groen et al. [24,25]. Parent TS-1-P samples were treated with TPAOH and NaOH solution of 0.2 M hydrothermally at 170 °C for 72 h. Afterwards, the slurry was cooled down immediately using an ice bath, separated by centrifugation, and washed with de-ionized water until neutral. Following that, TPAOH modified sample was calcined in air at 550 °C for 8 h and denoted as TS-1-O. While NaOH treated sample was ion exchanged with 1 M NH_4NO_3 solution at 80 °C for 24 h to fully exchange with NH_4^+ and then calcined in air at 550 °C for 8 h.

2.2. Catalyst characterization

X-ray diffraction patterns of the samples were recorded on a Bruker D8-Advanced X-ray diffract meter with Cu-Ka radiation ($\lambda = 1.54056$ Å) operating at 40 KV, 40 mA. Data were collected in the range of $2\theta = 5$–$50°$ at a scanning speed of 5°/min. The chemical composition of all samples was measured by X-ray Fluorescence (XRF) with a Bruker S4 Pioneer Spectrometer. N_2 adsorption was performed on a Quantachrome Autosorb-1 instrument at −196 °C, after a vacuum pretreatment at 300 °C for 6 h. Total specific surface area and pore volume were calculated by the BET and BJH methods. Micropore area and micropore volume were determined by the t method.

The morphology of the samples was examined by a combination of Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). TEM images were acquired by JEM-2100F (JEOL, 200 kV, 0.14 nm of resolution) and samples were prepared by dipping a sonicated suspension in ethanol on a carbon-coated copper grid. SEM images were obtained with Hitachi S-4800 scanning electron microscope (FE-SEM, 15 kV). To prepare the samples for SEM, a drop of dilute colloidal solution was placed onto the sample stud surface. Shortly before an SEM image is acquired, the sample was coated with gold.

The UV–vis absorbance spectra of the parent and as-synthesized samples were collected in a Lambda 750 spectrophotometer (Perkin-Elmer). Spectra were taken in the wavelength range of 190–800 nm at a scanning speed of 400 nm/min with data interval of 1 nm. FT-IR spectra of the samples were tested in the region 400-4000 cm^{-1} using a Nicolet 380 spectrometer.

The acidity of the samples was studied by temperature-programmed desorption of ammonia (NH_3-TPD) and FT-IR spectra of adsorbed pyridine. NH_3-TPD measurement was carried out on a conventional apparatus with an on–line thermal conductivity detector (TCD). In a typical test, 0.1 g catalyst placed in a quartz tube was heated at 550 °C in a flow of high purity N_2 for 2 h, then cooled down to ambient temperature. After that, sufficient NH_3 was introduced into the system through a six–way valve. Physically adsorbed NH_3 was removed by flushing with N_2 at 100 °C for 2 h and desorption was performed by heating the sample from 100 to 550 °C at a rate of 15 °C/min.

FT-IR spectra of adsorbed pyridine was performed using a Nicolet 380 spectrometer device at a resolution of 4 cm^{-1}. The sample powder was pressed into a self–supporting wafer (15 mg, 13 mm) and activated at 500 °C for 2 h under vacuum (10^{-3} Pa). Probe molecules were adsorbed in situ at room temperature and then evacuated at 200 °C for 1 h. Afterwards, an IR spectrum was recorded at room temperature and its difference spectrum was obtained by subtracting the spectrum of the activated sample from the spectrum after probe adsorption.

2.3. Catalytic performance evaluation

Gas-phase isomerization of styrene oxide was carried out in a continuous flow fixed-bed reactor (stainless steel tube, i.d. = 9 mm). The reactor was loaded with 0.5 g catalyst (20–30 mesh) and the reaction temperature was monitored by a K-type thermocouple which placed in the middle of the catalyst bed. In a typical reaction, the catalyst located in the constant-temperature zone was pretreated at 500 °C for 2 h and then cooled to reaction temperature (200 °C). N_2 was used as the carrier gas with a flow rate of 120 ml/min. Styrene oxide (>98%), free of any solvents, was pumped into the reactor by a micro liquid pump with WHSV = 3.0 h^{-1}. The products were collected in an ice trap and analyzed by GC (Agilent 6820, FID) and GC-MS (Agilent 6890/5973, MSD). The capillary column of VF-5 ms (30 m, 0.25 mm, 0.25 μm) was used for analyzing. Blank experiments were performed using the same experimental conditions without catalyst.

After reaction, the reactor was purged with N_2 at 200 °C for 2 h to remove any possible residual reactants. The weight loss of the spent catalysts was determined by a PerkinElmer, Pyris 6 Thermo Gravimetric Analyzer under an air flow-rate of 100 ml/min, with a heating rate of 10 °C/min from 30 to 800 °C.

3. Results and discussion

3.1. Physicochemical properties

As shown in Fig. 1, all the XRD patterns of the tested samples matched well with MFI-type structures and no new phase emerged [29]. The relative crystallinity was calculated by comparing the peaks' area of $2\theta = 22$-$25°$ of the prepared samples with that of highly crystalline TS-1-P sample, whose relative crystallinity was regarded as 100%. The intensity of TS-1-nano (104%) is close to that of TS-1-P, suggesting that the crystal size has little influence on crystallinity. A significant reduction in the intensity of the diffraction reflections is clearly observed for TS-1-N material (reduces to 71%), which can be attributed to its framework collapse. This implies that post-treatment with NaOH at the stated conditions destroyed the framework structure irreversibly. Interestingly, the relative crystallinity of TS-1-O (101%) increases rather than decreases relative to TS-1-P, showing that the long-range crystallinity can be preserved under suitable treatment conditions. The Si dissolution in TPAOH is more controllable than in NaOH, which might be associated with the pH differences [22]. This is probably