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Short Communication

Effect of TS-1 treatment by tetrapropyl ammonium hydroxide on cyclohexanone ammoximation

Xiaoxue Wu, Yaquan Wang *, Teng Zhang, Shuhai Wang, Pengxu Yao, Wenping Feng, Yi Lin, Juan Xu

Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, PR China

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ABSTRACT

TS-1 has been treated with different concentrations of tetrapropyl ammonium hydroxide (TPAOH), characterized by a series of techniques, and studied in cyclohexanone ammoximation. The results show that the MFI structure of TS-1 is not destroyed, while mesopores are formed in TS-1 crystals and the pore diameters increase with the TPAOH concentrations; the amount of the framework Ti species decreases slightly at low concentrations of TPAOH, but decreases appreciably at the concentrations of TPAOH above 0.0125 mol/L; the activity and the selectivity of TS-1 are not affected by the treatment, but the catalyst stability is markedly increased after the TPAOH treatment. The increase of the stability is attributed to the mesopore formation. But when the pore diameters are larger than 6.51 nm, the catalyst stability begins decreasing due to the appreciable damage of the framework titanium by TPAOH.

1. Introduction

Cyclohexanone oxime is the key intermediate for the manufacture of ε-caprolactam in the production of nylon-6 [1]. In 1988, Enichem Corporation reported a new process for producing cyclohexanone oxime from the ammoximation of cyclohexanone with NH_3 and H_2O_2 catalyzed by titanium silicalite (TS-1) [2]. The new process has nearly complete conversion of cyclohexanone and very high selectivity to oxime with lower energy consumption compared with the method through hydroxylamine [3]. This process has been widely investigated [4–8].

The catalyst stability of TS-1 in the reaction of cyclohexanone ammoximation is the key problem for the industrial use. Lin et al. [9] improved the catalyst stability through creating hollow cavities in TS-1 by treating the zeolite with organic-base, and called the catalyst as HTS-1 [10]. Wang et al. [11] characterized the HTS-1 obtained by treating TS-1 with tetrapropyl ammonium hydroxide (TPAOH), and found that the treatment also led to the increase of the catalytic activity in the reaction of the hydroxylation of phenol with H_2O_2, and the improved performance was ascribed to the formation of mesopores in TS-1. This process has been widely investigated [12–14]. The above reports indicated that the improved catalytic performance of TS-1 is attributed to the formation of mesopores, however it was not shown how large the mesopores are most suitable to the reactions.

In this work, TS-1 is treated by different concentrations of TPAOH. The catalytic performances of the TPAOH treated TS-1 are compared with those of the untreated TS-1 to study the effect of TPAOH concentrations, and therefore the dimensions of the mesopores, on TS-1 catalytic stability in the reaction of cyclohexanone ammoximation.

2. Experiment

2.1. Synthesis of TS-1

TS-1 was prepared following the procedure described in reference [15,16] with modification [17]. A solution of 5.12 g tetrabutyl titanate, 23.7 g dried isopropanol and 94.5 g tetraethyl orthosilicate were dropwisely added into a 149.41 g solution of 15 wt.% TPAOH in water in 90 min with vigorous stirring under N_2 atmosphere. Then the mixture was heated to 80 °C and kept at this temperature for 3 h to remove ethanol, isopropanol and butanol. The resulting mixture with the following molar composition: SiO_2:0.034TiO_2:0.24TPAOH:26.3H_2O was transferred into a 300 mL PTFE lined stainless steel autoclave and crystallized at 170 °C for 72 h under static conditions. After cooling to room temperature, the crystalline product was obtained by filtration, washed with deionized water to pH = 7, dried at 120 °C for 6 h, and finally calcined at 550 °C in air for 6 h.

2.2. Treatment of TS-1 with TPAOH

The obtained TS-1 was treated with TPAOH at different concentrations. 1 g TS-1 was dispersed in a solution of x mol/L TPAOH, with x varied at 0, 0.00416, 0.00832, 0.0125 and 0.0166, respectively. The mass ratio of liquid/TS-1 was 36. After vigorously stirred for 20 min, the mixture was transferred into a PTFE lined stainless-steel autoclave and heated at 170 °C for 24 h. The autoclave was then rapidly cooled and the zeolite was separated by centrifugation, washed with distilled

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* Corresponding author. Tel.: +86 22 23507881.
E-mail address: yqwang@tju.edu.cn (Y. Wang).

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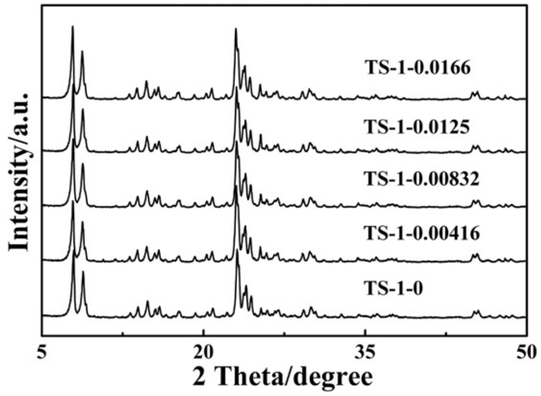

Fig. 1. XRD patterns of untreated TS-1 and TS-1 treated with different concentrations of TPAOH.

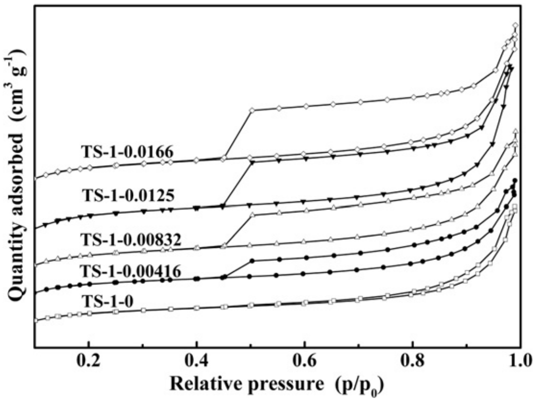

Fig. 2. N2 adsorption/desorption isotherms for untreated TS-1 and TS-1 treated with different concentrations of TPAOH.

water to pH = 7, dried at 120 °C overnight, and then calcined at 550 °C in air for 6 h. The samples are named as TS-1 − x, where x is the molar concentration of TPAOH.

2.3. Characterization

X-ray powder patterns (XRD) were obtained on a Rigaku D/max 2500 diffractometer. N_2 adsorption/desorption isotherms were obtained on a Micromeritics TriStar 3000 apparatus. The specific surface areas, pore sizes and pore volumes were calculated with BET equation, BJH method and *t*-plot, respectively. The FT-IR and UV–Vis of the samples were obtained on Bruker Vertex 7.0 spectrometer and Hitachi U-3010 spectrometer, respectively. Nanosem 430 field emission scanning electron microscopy (SEM) was used to characterize the sizes and morphology of the samples.

2.4. Ammoximation of cyclohexanone

The catalytic performance of TS-1 on cyclohexanone ammoximation was studied in a 150 mL three-neck glass flask reactor equipped with a filter to keep the catalyst in the reactor. Typically, 0.5 g TS-1 catalyst powder and 90 g *t*-butanol were introduced into the reactor. The mixture was mildly stirred and heated to 76 °C. Then the ammonia gas and the mixed water solution of cyclohexanone/*t*-butanol/H_2O_2 were added into the reaction system controlled by a mass flow controller and a micropump, respectively. The weight hourly space velocity (WHSV) of cyclohexanone was always kept at a high value to differentiate the catalysts lives quickly, i.e., 36 g cyclohexanone per gram catalyst per hour. The molar ratios of *t*-butanol/cyclohexanone, H_2O_2/cyclohexanone and NH_3/cyclohexanone were 3.33, 1.10 and 2.00, respectively. The products were collected in a glass container and analyzed on a gas chromatography (GC-SP-3420A) every hour.

3. Results and discussion

3.1. Characterization of untreated TS-1 and TS-1 treated with different concentrations of TPAOH

The X-ray diffraction patterns of the untreated TS-1 and TS-1 treated with different TPAOH concentrations are shown in Fig. 1. The five characteristic reflections of MFI topology at $2\theta = 7.9°, 8.8°, 23.1°, 23.9°$ and 24.4° appear in the patterns as widely reported in the literature [18,19]. In addition, the single peak at 24.4° indicates a change from monoclinic symmetry to orthorhombic symmetry of TS-1, agreeing with those reported for TS-1 in the literature [19]. There is no clear difference in the intensity of the diffractions for all the samples, indicating that the post-treatment with TPAOH does not destroy the MFI framework structure.

Fig. 2 shows the nitrogen physical adsorption isotherms of TS-1 samples. A hysteresis loop appears in each isotherm of the treated samples, indicating the generation of mesopores in the crystals. The BET specific surface areas, pore volumes and pore diameters are listed in Table 1. Compared with those of the untreated TS-1, the BET specific surface areas do not change appreciably, whereas the mesopore volumes and pore diameters increase appreciably. By increasing the TPAOH concentration from 0.00416 mol/L to 0.0166 mol/L, the V_{meso} and pore diameters increase from 0.174 cm^3/g and 6.28 nm, respectively, to 0.221 cm^3/g and 7.47 nm, respectively, while for the untreated TS-1 samples, the V_{meso} and pore diameter are only 0.168 cm^3/g and 5.99 nm, respectively. No clear difference is found in the micropore volume for all the samples. The increase of mesopore volumes and pore diameters is probably due to the dissolution from inside of the TS-1 crystals in the basic solution.

The FT-IR spectra of untreated TS-1 and TS-1 treated with different concentrations of TPAOH are shown in Fig. 3(a). The main adsorption bands are observed at 550, 800, 960, 1100 and 1230 cm^{-1} in IR spectra of all samples, which agree with the typical FT-IR spectra of TS-1 reported in the literature [20]. The band at 960 cm^{-1} in IR spectra indicates the presence of Ti atoms in tetrahedral coordination within the silicalite framework and the intensity of this band is related to the content of titanium in the framework [21]. Appreciable decrease is found on the intensity of the band at 960 cm^{-1} with increasing the TPAOH concentrations, indicating the loss of the framework Ti species.

The Ti coordination state of TS-1 is investigated with UV–Vis diffuse reflectance and the results are given in Fig. 3(b). All samples show similar spectrum. Two major peaks are found at 210 nm and 330 nm which are assigned to tetra-coordinated titanium in the zeolite framework and

Table 1
BET specific surface areas, pore volumes and pore diameters of untreated TS-1 and TS-1 treated with different concentrations of TPAOH.

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	Pore diameter (nm)	Particle sizes (nm)
TS-1-0	408	0.110	0.168	5.99	216
TS-1-0.00416	397	0.115	0.174	6.28	211
TS-1-0.00832	406	0.113	0.187	6.51	218
TS-1-0.0125	398	0.115	0.206	6.92	216
TS-1-0.0166	405	0.116	0.221	7.47	212