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Short communication

Hierarchical TS-1 synthesized via the dissolution-recrystallization process: Influence of ammonium salts

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ABSTRACT

TS-1 was post-modified by ammonium salts or tetrapropylammonium hydroxide (TPAOH). During the ammonium salts modification, the crystals were eroded and extra-framework titanium species were formed. After the combined-modification, hierarchical TS-1 with secondary pore volume in the 0.22–0.28 cm^3/g range was obtained via the intensified dissolution-recrystallization process, although more extra-framework titanium species were generated as five-/six-coordinated species. In cyclohexene oxidation with *tert*-butyl hydroperoxide (TBHP) as the oxidant, the activity of modified TS-1 decreased when anatase was formed only. However, it increased in the presence of five-/six-coordinated titanium. The secondary porosity further improved the catalytic performance and the activity of the combined-modified TS-1 samples increased remarkably by > 100%.

1. Introduction

Zeolites frameworks are usually consisted of silicon and aluminum atoms. When some of the framework silicon/aluminum atoms are substituted by heteroatoms, such as titanium, tin and zirconium, heteroatom zeolite is synthesized. TS-1 is one of the most important heteroatom zeolites, in which titanium is isomorphously substituted into the framework. Due to the excellent performance in alkene and allylic compounds epoxidation [1–6], cyclohexanone ammoximation [7], phenol hydroxylation [8,9] and oxidative desulfurization [10], lots of works on the synthesis, characterization and application of TS-1 have been carried out since it was firstly reported in 1983 [11]. However, the pore size of TS-1 is only about 0.55 nm, which is too small for the reactants with larger molecular size to access the active centers within the channels. To enhance the activity in reactions with larger substrates (> 0.55 nm) over TS-1 solids, the accessibility of the active sites inside the TS-1 crystals should had been improved by introducing super-micropores, mesopores and macropores, thus hierarchical TS-1 (HTS) structures were prepared [12–19].

A variety of strategies, such as dissolution-recrystallization (DR) [12,13], desilication [14], dry-gel conversion [15], templating [16,17] and silanization [18,19] were efficient in the synthesis of HTS. Thereinto, the DR technology was able to simultaneously improve the activity, selectivity and lifetime [20]. Lin et al. [12] treated TS-1 with quaternary ammonium hydroxide, and an HTS with intracrystalline voids and better activity and stability was obtained. Although the HTS has been successfully used in the industrial production of cyclohexanone oxime and propylene oxide, the synthesis process was supposed to be influenced by the OH^- diffusion in the TS-1 crystals. During the DR process, the OH^- species could diffuse into the channels and erode the inner part of the crystals. However, the tetrapropyl ammonium cations (TPA^+, 0.84 nm) and tetrabutyl ammonium cations (TBA^+, 1.04 nm) are too large to enter by diffusion [21]. Considering the charge balance effect, the OH^- diffusion and the dissolution process are both restrained. To overcome this constraint, NaOH [22] or $NH_3{\cdot}H_2O$ [23] has been used with tetrapropyl ammonium hydroxide (TPAOH), and positive effects were found. In the presence of TPAOH and $NH_3{\cdot}H_2O$, the DR process is intensified, and HTS with larger mesopore volume (V_S, larger than 0.18 cm^3/g) was prepared more efficiently, which improved the accessibility of the active sites [23]. When NaOH is used, HTS with much larger V_S (0.20–0.27 cm^3/g) is achieved. However, Na^+ exerts negative influence on the Ti re-incorporation, and the extra-framework titanium content increases [22].

In order to further improve the efficiency of DR technology, ammonium salts, including $(NH_4)_2CO_3$, NH_4Cl and $(NH_4)_2SO_4$, were introduced into the DR process in the present work; besides, the ammonium salts modification was also conducted. The influences of the post-modification on the physicochemical properties were studied, and the catalytic activity of the modified TS-1 was evaluated for the cyclohexene (0.62 nm) epoxidation with *tert*-butyl hydroperoxide (0.64 nm)

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as oxidant.

2. Experimental

2.1. Catalyst preparation

TS-1 was synthesized as follows [22,23]: The molar ratio of the corresponding precursor compounds SiO_2:TiO_2:TPAOH:H_2O was 1:0.02:0.4:50. TS-1 was post-modified by aqueous $(NH_4)_2CO_3$, NH_4Cl, $(NH_4)_2SO_4$ or a mixed solution of TPAOH with the ammonium salts. The ammonium salts were dissolved in deionized water or aqueous TPAOH, their total molar concentration was 0.1 mol/L, while the TPAOH concentration was 0 or 0.4 mol/L. 2 g TS-1 was mixed with 20 mL of the solution. The solution mixture obtained was transferred to a teflon-lined stainless-steel autoclave, and the post-synthesis was carried out under autogenous pressure at 150 °C for 36 h. The product was filtered, washed with distilled water, dried at 100 °C for 12 h, and then calcined at 550 °C for 4 h. The samples obtained in the combined modification were denoted as TS-1-P-M, while TS-1-M was used to illustrate the samples modified with aqueous ammonium salts; P and M, respectively, represent TPAOH and the additive agents.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were collected on a Philips Panalytical X'pert diffractometer with nickel-filtered Cu Kα radiation, and lattice parameters were derived by Rietevield analysis. X-ray fluorescence (XRF) experiments were conducted on a Rigaku 3721E spectrometer with W radiation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded, respectively, on a Hitachi 4800 and a JEOL JEM-2100 microscope. N_2 adsorption-desorption isotherms (77 K) were measured on a Micromeritics ASAP 2405 apparatus, and textural properties were derived from the isotherms using the BET and *t*-plot methods. Infrared (IR) spectra were recorded on a Thermo Nicolet 750 infrared spectrometer, and UV–visible diffuse reflectance (UV–Vis/DR) spectra were recorded on a JASCO UV–visible 550 spectrometer.

2.3. Catalytic activity

As the molecular sizes of cyclohexene and TBHP are both larger than the pore size of TS-1, the catalytic activity was evaluated towards the cyclohexene epoxidation reaction to illustrate the influences of the hierarchical porosity. The chemical equations describing the main and side reaction products obtained are given in Supplementary information. The reaction was carried out in a round-bottom flask equipped with a condenser and a magnetic stirrer. A 0.3 g catalyst sample was mixed with 6.24 g cyclohexene and 6.84 g TBHP (5.5 mol/L in decane), and the mixture was heated to 100 °C. After reaction for 2 h, the products were analyzed by an Agilent 6890 N gas chromatograph equipped with a FFAP capillary column, while the TBHP efficiency was analyzed by iodometric titration.

3. Results and discussion

3.1. Physiochemical properties

3.1.1. Influences of the ammonium salts modification

The chemical composition (SiO_2:TiO_2) and surface properties of the modified samples are given in Table 1. Although the pH values of the NH_4Cl, $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ solutions (0.1 mol/L) were respectively about 5.1, 5.5 and 9.2, and the silicon atoms on the surface or even in the framework could be removed by acid/base modification [24–26], the MFI topology remained unchanged (see Supplementary information, Fig. S1). Moreover, the SiO_2:TiO_2 ratio was almost the same after the ammonium salts modification, which might be a result of the flocculation effect of the ammonium salts. However, the specific surface area (S_{BET}), matrix area (S_{MA}), micropore area (S_{MI}), micropore volume (V_{MI}) and total pore volume (V_T) all decreased, which indicates that the TS-1 crystals were eroded by the modification applied. Comparatively, the erosion was much more severe under alkaline conditions, and the S_{MI} and V_{MI} values of TS-1-$(NH_4)_2CO_3$ are only 311 m^2/g and 0.139 cm^3/g, respectively.

Table 1
The chemical composition and surface properties of TS-1 and the modified samples.

Sample	SiO_2:TiO_2	Surface properties				
		S_{BET} (m^2/g)	S_{MA} (m^2/g)	S_{MI} (m^2/g)	V_{MI} (cm^3/g)	V_S (cm^3/g)
TS-1	49.3	457	43	413	0.190	0.078
TS-1-P	49.1	443	46	397	0.179	0.175
TS-1-$(NH_4)_2SO_4$	49.3	396	14	382	0.172	0.055
TS-1-P-$(NH_4)_2SO_4$	49.2	446	53	393	0.178	0.226
TS-1-NH_4Cl	49.5	413	19	394	0.174	0.073
TS-1-P-NH_4Cl	49.3	442	50	392	0.178	0.279
TS-1-$(NH_4)_2CO_3$	49.4	324	14	311	0.139	0.037
TS-1-P-$(NH_4)_2CO_3$	49.2	441	51	390	0.176	0.269

S_{BET}: the specific surface area, calculated by BET method.
S_{MA}: external surface area, calculated by t-method.
S_{MI}: microporous surface area, calculated by t-method.
V_{MI}: microporous volume, calculated by t-method.
V_S: secondary pore volume, subtraction of total pore volume and microporous volume.

The pore size distribution derived from the N_2 adsorption isotherms [27] (Fig. S2) of TS-1 and modified TS-1 are shown in Fig. 1. Although the TS-1 crystals were eroded, there are no hysteresis loops in the isotherms, and the population of mesopores with sizes in the 2–8 nm range decreases.

The SEM images (Fig. S3) illustrate that the TS-1 particles are about 400 nm, and consist of aggregates of small crystals with sizes of about 50–100 nm. The surface of TS-1 is smooth, which remains relative smooth after NH_4Cl and $(NH_4)_2SO_4$ modification. For the TS-1-$(NH_4)_2CO_3$, grooves on the surface are observed, which further illustrate that the TS-1 crystals are eroded more severely by the use of aqueous $(NH_4)_2CO_3$.

Fig. 2 shows the FT-IR spectra of solids investigated. The characteristic peak at 960 cm^{-1} is assigned to the stretching vibration mode of Si—O in the Si—O—Ti bridges [28]. Although the TS-1 crystals were eroded by the ammonium salts, Ti is still in the framework of the modified samples.

The UV–Vis/DR spectra of the solids investigated are illustrated in Fig. 3. The characteristic bands of the four-coordinated framework titanium ions, the five- or six-coordinated extra-framework titanium species (FSEFT), and those of anatase are respectively at about 210 nm, 270–290 nm and 330 nm [29–31]. As for the parent TS-1, the titanium species were mainly in the framework position. Most of the titanium in the modified samples is still regarded as four-coordinated, but anatase was formed because of erosion. Besides, FSEFT were also introduced by $(NH_4)_2CO_3$ for the more severe erosion. As the Ti—O and Si—O bonds in TS-1 were respectively about 1.80 Å and 1.61 Å [32], the cell parameters decreased with decreasing framework titanium content (Table S1).

3.1.2. Influences of the combined-modification

HTS with intracrystalline voids were synthesized via the DR process by post-modification with TPAOH. When NaOH or $NH_3{\cdot}H_2O$ was introduced, HTS with larger Vs could be prepared [22,23]. In the presence of both TPAOH and ammonium salts, the combined modification exerted little influences on the chemical composition, where the SiO_2:TiO_2 of TS-1-P-NH_4Cl, TS-1-P-$(NH_4)_2SO_4$ and TS-1-P-$(NH_4)_2CO_3$ were all about 49.2, which was almost the same as that of parent TS-1.