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Article

Hydrothermal synthesis and catalytic performance of bulky titanium silicalite-1 aggregates assembled by bridged organosilane

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ABSTRACT

A facile and effective method to synthesize TS-1 zeolite aggregates has been presented. The crystallization of silanized seeds and nanocrystallites led to large and irregular TS-1 zeolite aggregates ranging from 5 to 40 μm in size, based on the special sol-gel chemistry of bridged organosilane. Epoxidation of 1-hexene and cyclohexene was used as a probe reaction to investigate the catalytic performance of the resulting materials. These TS-1 zeolite aggregates possessed both the conventional nanoparticle properties of TS-1 zeolites and variable surface hydrophilic/hydrophobic features, which enhanced the catalytic properties of hydroperoxides for alkene epoxidation. Moreover, the large aggregates effectively simplified the separation procedure during preparation and catalytic reactions.

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1. Introduction

TS-1, a typical zeolite with an MFI structure, has attracted much attention because of its high importance in catalysis for the selective oxidation of various organic compounds using H_2O_2 as an oxidant under mild conditions [1–3]. However, TS-1 suffers from intracrystalline diffusion limitations due to its relatively small pore size. Nanosized zeolite materials have a number of advantages as compared to TS-1 with a large size [4]. For example, the abundant active sites on their external surface are accessible by large substrate molecules in the reactions, since the decrease in crystal size reduces intracrystalline diffusion limitations. Similarly, the deactivating effect caused by coke deposition is less pronounced when using zeolite nanocrystals [5].

However, zeolites with sizes below 100 nm are usually accompanied by a separation problem. To solve the separation

problem, considerable efforts have been devoted to disperse zeolite nanocrystals in an inert matrix [6] or to shape zeolite nanocrystals into aggregates [7–9]. In general, larger zeolite aggregates could be achieved by the use of polystyrene beads [10–12], anion-exchange resin beads [13,14], silylated polymers [15], and polymerization-induced colloid aggregation (PICA) [16]. Alternatively, silanization is a fascinating method to prepare zeolites with hierarchical porosity. The introduction of organic fragments into zeolites using organosilanes has been widely reported in the literature [17–33], which imparts the zeolites very high hydrophobicity and various functionalities. Choi *et al.* [26,27] synthesized a crystalline zeolite with tunable mesoporosity by adding a rationally designed amphiphilic organosilane surfactant into conventional alkaline zeolite synthesis mixtures. Serrano *et al.* [28–32] found that the silanization of zeolitic seeds could lead to hierarchical ZSM-5 zeolites and other zeolites, where the organic moiety nature greatly affected

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the size of the zeolitic nanounits and mesoporosity [29,30]. The organosilane species with a Si–C bond anchored onto the surface of zeolite nanoseeds could partially inhibit further aggregation of the nanoparticles into larger crystals during zeolitization, resulting in hierarchical zeolite products with a large surface area [28–30]. Hexadecyltrimethoxysilane and 1,8-bis(triethoxysilyl)octane organosilanes have also been applied to tailor hierarchical beta zeolites by modified orientated attachment growth *via* the dry-gel conversion approach [34]. However, the prepared zeolites aggregates were still very difficult to be separated and recovered as aggregates with small sizes ranging from 300 to 500 nm [29,30]. Therefore, macrosized aggregates possessing the properties of nanosized zeolites, as well as easy disposal and recovery are expected.

Herein, a bridged organosilane, 1,8-bis(triethoxysilyl)octane, was used as a silanization agent to assemble TS-1 nanoseeds and nanocrystallites with sizes of ~100 nm into large aggregates. The size of the obtained TS-1 aggregates was in the range 5–40 μm , which was about two orders of magnitudes larger than that obtained using organotrialkoxysilanes [26,27,34]. These bridged organosilanes could be effectively anchored onto the zeolitic units and perturbed subsequent crystal growth, and thus successfully bridged/assembled zeolite seeds and nanocrystallites to bulky aggregates. The TS-1 aggregates were robust enough to suffer continuous ultrasonication for 1 h or more without any destruction, indicating that the zeolite materials could curtail the filtration difficulties during preparation and recovery in catalytic applications. Epoxidation of alkene using aqueous H_2O_2 as an oxidant was chosen as a probe reaction to evaluate the performance of the obtained TS-1 aggregates and the conventional nanoscale TS-1. The results indicated that the hierarchical TS-1 zeolite aggregates showed good catalytic performance in the epoxidation of cyclohexene.

2. Experimental

2.1. Chemicals

The chemicals used in this work were as follows: tetraethylorthosilicate (TEOS, AR, SCRC), tetrapropylammonium hydroxide (TPAOH, 25 wt%, Sigma-Aldrich), tetrabutylorthotitanate (AR, SCRC), 1,8-bis(triethoxysilyl)octane (AR, Sigma-Aldrich), H_2O_2 (30 wt%, SCRC), 1-hexene and cyclohexene (AR, Sigma-Aldrich), methanol (AR, SCRC), and $\text{Ce}(\text{SO}_4)_2$ (AR, SCRC).

2.2. Materials synthesis

In a typical synthesis, seeds were presynthesized by pre-crystallization of the precursor gel with a molar composition of 1 SiO_2 :0.025 TiO_2 :0.3 TPAOH:20 H_2O at 100 $^\circ\text{C}$ for 24 h. The seeds were subsequently crystallized at 175 $^\circ\text{C}$ for 72 h as a reference sample (denoted as TS-S-(0)). The TS-1 nanocrystallites were obtained with a molar composition of 1 SiO_2 :0.025 TiO_2 :0.3 TPAOH:20 H_2O , and then treated at 175 $^\circ\text{C}$ for 72 h as the other reference sample (denoted as TS-C-(0)). The

as-synthesized zeolitic seeds/nanocrystallites were functionalized by adding a bridged organosilane. The mixture was stirred at 105 $^\circ\text{C}$ for 4–6 h. The functionalized seeds/nanocrystallites were subsequently crystallized at 175 $^\circ\text{C}$ for 72 h. The samples obtained from the seeds were denoted as TS-S-(X), and those obtained from the crystallites were denoted as TS-C-(X), where X indicates the molar ratio of 1,8-bis(triethoxysilyl)octane/ SiO_2 . All the calcined samples were treated with 0.5 mol L^{-1} HCl at 80 $^\circ\text{C}$ for 2 h before they were used in the catalytic reaction.

2.3. Characterization

Powder X-ray diffraction patterns (XRD) of the samples were recorded on a Rigaku Ultima IV X-Ray diffractometer over the 2θ range from 5 $^\circ$ to 35 $^\circ$. Scanning electron microscopy (SEM) images were obtained on a HITACHI S-4800 system at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) characterization was carried out on an FEI Tecnai G² F30 instrument operating at 300 kV. For the TEM images, the specimens were dispersed in ethanol and placed on holey copper grids. Nitrogen adsorption-desorption measurements were carried out at –196 $^\circ\text{C}$ on a nitrogen adsorption apparatus (Quadrachrome evo). The surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) method. The total pore volume was estimated from the amount of nitrogen adsorbed at the relative pressure (p/p_0) of 0.95, and the micropore volume was calculated from the t -plot method. Ultraviolet-Visible (UV-Vis) spectra were recorded on a Shimadzu UV-2550 spectrometer using BaSO_4 as the reference. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of the as-prepared zeolites were performed on a METTLER TOLEDO TGA/SDTA851 apparatus; the measurements were carried out in flowing air (5 $\text{cm}^3 \text{min}^{-1}$) at a heating rate of 10 $^\circ\text{C min}^{-1}$. ^{29}Si solid-state MAS NMR spectra were recorded on a Varian VNMR-400WB spectrometer.

2.4. Catalytic tests

The epoxidation of 1-hexene and cyclohexene using aqueous H_2O_2 as an oxidant was carried out in a 50-mL round-bottomed flask immersed in a thermostatic oil bath equipped with a condenser. 0.05 g of the catalyst, 10 mL of methanol, 10 mmol of 1-hexene or cyclohexene, and 10 mmol hydrogen peroxide (30 wt% H_2O_2 aqueous solution) were successively charged into the reactor. The reaction was carried out under vigorous stirring, and the temperature was controlled at 60 $^\circ\text{C}$ for 2 h. After the reaction, the reactants were cooled quickly, and 0.5 g cyclohexanone (internal standard) was added to the flask and stirred for 1 min. After removal of the catalyst powder, the reaction mixture was analyzed using a gas chromatograph (capillary column, FID detector). The amount of unconverted H_2O_2 was determined using a 0.1 mol L^{-1} aqueous solution of $\text{Ce}(\text{SO}_4)_2$ by a titration method.

3. Results and discussion

Fig. 1. Powder XRD patterns of the as-synthesized seed (1), TS-S-(0) (2) TS-S-(0.05) (3), TS-C-(0) (4), and TS-C-(0.1) (5) zeolites.

The XRD patterns (Fig. 1) showed that all the samples exhibited the characteristic diffraction peaks of the MFI structure, although their diffraction intensities were slightly different. This indicated that the introduction of the bridged organosilane did not change the characteristic structure of the zeolite. The peak intensities of TS-S-(0) and TS-C-(0) were analogous, and they were obviously higher than those of the TS-1 seed gel crystallized at a low temperature (100 °C). This indicated that there was more amorphous silica in the TS-1 seed gel. The intensity of the diffraction peaks of TS-S-(0.05) and TS-C-(0.1) obtained by adding 1,8-bis(triethoxysilyl)octane decreased as compared with that of the reference samples (TS-S-(0) and TS-C-(0)), which was attributed to crystal growth inhibition in the presence of organosilanes in the second step [35]. The introduction of 1,8-bis(triethoxysilyl)octane led to the appearance of amorphous silica in the TS-S-(0.05) and TS-C-(0.1) samples. With the increase in the amount of 1,8-bis(triethoxysilyl)octane, the diffraction peak intensity of the obtained samples gradually decreased, as shown in Fig. S1.

As shown in Fig. 2 and Fig. S2, the TS-S-(0) and TS-C-(0) samples prepared without 1,8-bis(triethoxysilyl)octane comprised crystals with a mean dimension of around 100–150 nm. These could not be directly recovered by conventional filtration. However, all the as-prepared silanized zeolite samples could be easily recovered by filtration. These silanized zeolite samples consisted of large and irregular aggregates ranging from 5 to 40 μm in size, which was different from the morphology reported in the literature [28–31]. Meanwhile, all these aggregates consisted of primary zeolitic nanoparticles with sizes of about 120–200 nm, and zeolitic nanoparticles were clearly observed and did not grow into large crystals. Compared with the organosilanes with a single alkyl substituent, the bridged organosilane played a very important role in the macroscopic morphology of the hierarchical zeolite aggregates, similar to that reported elsewhere [34]. Although 1,8-bis(triethoxysilyl)octane was also used to assemble the zeolite beta precrystallized gel, the size of the zeolite beta aggregates was only about 200 nm, which might still be difficult to separate [34]. The TEM images (Fig. 2(c) and 2(g)) showed that the aggregates were assembled by nano-TS-1 zeolites. 1,8-Bis(triethoxysilyl)octane covered the surface of the seeds/crystallites with two condensable heads (Fig. 2(d) and 2(h)), which was also analogous to that reported in the literature [34]. There were many intracrystalline irregular voids with sizes of 3–10 nm in the TS-1 aggregates, and the high-magnification TEM images showed that the zeolite nanocrystals were linked by amorphous silica, which was consistent with the XRD results. 1,8-Bis(triethoxysilyl)octane acted as an agglomerant and inhibitor for further growth. The overall key scheme of the formation of TS-1 zeolite aggregates is illustrated in Scheme 1. When bridged organosilanes were added to the as-synthesized zeolitic seeds or/and zeolitic crystalline solutions, the as-synthesized zeolitic seeds/nanocrystallites were functioned by the bridged organosilanes under the conditions of hydrothermal crystallization. Then, the zeolitic seeds/nanocrystallites could be assembled into nanocrystal

Fig. 2. SEM images of the as-synthesized TS-S-(0) (a), TS-S-(0.05) (b), TS-C-(0) (e), and TS-C-(0.1) (f) zeolites. TEM images of a single TS-S-(0.05) (c and d) and TS-C-(0.1) (g and h) aggregates.

Scheme 1. Proposed formation of hierarchically TS-1 using bridged organosilanes as the agglomerant and inhibitor.

Table 1

Textural properties and mass loss of the TS-1 samples.

Sample	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	S_{EXT} ($\text{m}^2 \text{g}^{-1}$)	S_{Mic} ($\text{m}^2 \text{g}^{-1}$)	V_{Mic}^b ($\text{cm}^3 \text{g}^{-1}$)	V_{total}^c ($\text{cm}^3 \text{g}^{-1}$)	Mass loss (%)
TS-S-(0)	423	156	267	0.14	0.30	13.1
TS-S-(0.05)	428	167	261	0.13	0.31	16.9
TS-C-(0)	429	172	257	0.14	0.32	13.9
TS-C-(0.1)	428	176	252	0.13	0.27	20.6

^a surface area, calculated by BET method

^b micropore volume, calculated by *t*-plot method

^c total pore volume at $p/p_0 = 0.95$.

aggregates where bridged organosilanes covered the surface of seeds/crystallites with two condensable heads.

TG analysis was used to demonstrate the incorporation of 1,8-bis(triethoxysilyl)octane. The TG profile showed a total mass loss of 13.1%–20.6% from room temperature to 800 °C (Table 1 and Fig. 3). The mass loss of the silanized TS-1 with 1,8-bis(triethoxysilyl)octane was obviously larger than these of the TS-S-(0) and TS-C-(0) samples. For TS-S-(0) and TS-C-(0), the first step below 200 °C was associated with the desorption of water, and the second step between 200 and 500 °C was associated with the decomposition of TPA^+ [36]. In the case of the TS-S-(0.05) and TS-C-(0.1) aggregates, the mass loss at

200–500 °C was derived from the decomposition of both TPA^+ and 1,8-bis(triethoxysilyl)octane. The TG results further indicated that 1,8-bis(triethoxysilyl)octane was successfully assembled on the TS-1 zeolite, which was consistent with the conclusions based on TEM observations.

Since this method was based on the silanization of zeolite seeds and crystallites, one of the most important points for determining the morphology of the zeolite aggregates is the hydrolysis and condensation of the bridged organosilanes. Therefore, the effects of silanization temperature, structure of organosilanes with different carbon chains, concentration of TPAOH , and introduction of alcohol on the hydrolysis and condensation of the bridged organosilanes was investigated in detail. A model molar composition of the synthetic mixtures (TS-C-(0.1)) as the basis was analyzed.

Bridged organosilanes could be hydrolyzed and condensed under relatively mild conditions that are typical for sol-gel polymerization [37,38], and the sol-gel process could greatly influence the zeolite morphology. As shown in Fig. S3, when silanization was carried out at lower temperatures (40–90 °C), some large and smooth blocks were derived from the self-hydrolysis and condensation of the bridged organosilane, and no relatively uniform zeolite aggregates were formed. Oviatt *et al.* [39] considered that the flexibility of alkylene spacers

Fig. 3. TG-DTG curves of TS-S-(0) (a), TS-S-(0.05) (b), TS-C-(0) (c), and TS-C-(0.1) (d) zeolites.

in a bridged organosilane could greatly influence the hydrolysis and condensation of such monomers and then the surface area and porosity of the resulting xerogels under both acidic and basic conditions. Bridged organosilanes with different carbon chains greatly influenced the macroscopic morphology of the zeolite aggregates. When bis(triethoxysilyl)ethane was used as a silanization agent instead, a rigid zeolite monolith linked by some amorphous silica was formed after the hydrothermal treatment at 175 °C for 3 d (Fig. S3 (C)). The concentration of TPAOH in the synthesis gel mixture could affect the hydrolysis and condensation of the bridged organosilane, and consequently, the assembled aggregate morphology of the zeolite. With increasing concentration of TPAOH, the zeolite aggregation was hindered (Fig. S4), which indicated that the hydrolyzation-condensation of the bridged organosilane could be controlled by TPAOH. Alcohol could affect the hydrolyzation of the bridged organosilane [40]. When an alcohol was added to the synthesis system, uniform and scattered zeolite entities could be observed (Fig. S5). Assembly between the zeolite and the bridged organosilane was favorable when the alcohol was evaporated, which was inconsistent with the results in the literature, where the alcohol addition increased the incorporation of the silanization agent onto the zeolite [40]. When increasing the alcohol content, no aggregates could be acquired. Therefore, careful manipulation of the sol-gel chemistry of bridged organosilanes could inhibit further growth of the nanoparticles into larger crystals and favor the control of the macroscopic morphology.

Nitrogen adsorption-desorption isotherms provided information on the textural properties of all the zeolite samples (Table 1). Combined Type IV & I isotherms, typical for microporous-mesoporous materials, were observed for all the samples (Fig. 4). The TS-1 samples prepared in presence of 1,8-bis(triethoxysilyl)octane possessed a micropore volume, external surface area, and micropore surface area similar to those of TS-1(0)-S and TS-1(0)-C, indicating that 1,8-bis(triethoxysilyl)octane did not significantly change the textural properties of the parent TS-1 material.

It is known that the Ti species in the framework positions are the active sites for the selective catalytic oxidation of hydrocarbons when using peroxides as oxidants. The effective

Fig. 4. Nitrogen adsorption-desorption isotherms of the TS-S-(0) (1), TS-S-(0.05) (2), TS-C-(0) (3), and TS-C-(0.1) (4) zeolites.

Fig. 5. UV-Vis spectra of the TS-S-(0) (1), TS-S-(0.05) (2), TS-C-(0) (3), and TS-C-(0.1) (4) zeolites.

incorporation of titanium into the zeolite framework was confirmed by UV-Vis spectra [41,42]. For the TS-1 samples prepared by seed silanization, a shift was observed at the edge of the band (centered at 220 nm) toward higher wavelengths possibly due to the penta- or hexacoordinated Ti sites located on the outer surface of the nanocrystallites [35]. Fan *et al.* [43] indicated that extremely pure reagents and elaborate control of the synthesis conditions would be necessary to synthesize TS-1 with a framework Si/Ti ratio lower than 40. The presence of extra-framework TiO_2 in these TS-1 samples could be related to the relatively high Ti content in the synthesis mixture [43,44]. Here, both the silanized-seed TS-1 zeolites and reference TS-1 samples gave an intense ligand-to-metal charge transfer band at around 220 nm and a small band at around 330 nm, corresponding to tetrahedral coordinated Ti (IV) species [45] and extra-framework TiO_2 [46], respectively. The addition of 1,8-bis(triethoxysilyl)octane did not affect the coordination of the Ti species (Fig. 5).

The structural configuration and the states of the Si species were further investigated by ^{29}Si MAS NMR. As shown in Fig. 6, the ^{29}Si MAS NMR spectra of all the TS-1 samples indicated a

Fig. 6. ^{29}Si MAS NMR spectra of as-synthesized TS-S-(0) (1), TS-S-(0.05) (2), calcined TS-S-(0.05) (3), TS-C-(0) (4), TS-C-(0.1) (5), and calcined TS-C-(0.1) (6) zeolites.

Table 2

Catalytic properties of the TS-1 samples.

Sample	Si/Ti in product	1-Hexene				Cyclohexene					
		Conv. (%)	Selec. (%) ^a	H ₂ O ₂ (%)		Conv. (%)	Selec. (%) ^c			H ₂ O ₂ (%)	
				Conv.	Effi. ^b		Epoxide ^d	Diol ^e	Ether ^f	Conv.	Effi. ^b
TS-S-(0)	45	22.5	98.5	23.2	93	2.7	32	30	32	3.3	83
TS-S-(0.05)	47	21.6	98.1	23.7	92	6.2	43	22	29	7.8	79
TS-C-(0)	42	21.2	98.4	22.8	93	2.8	30	29	33	3.4	82
TS-C-(0.1)	46	20.5	98.9	22.5	91	5.7	40	26	28	7.1	80

Reaction conditions: 60 °C, 2 h, catalyst 0.05 g, solvent 10 mL, alkene 10 mmol, H₂O₂ 10 mmol.^a Epoxide selectivity.^b Efficiency.^c Three main products were listed.^d Epoxycyclohexane.^e Dicyclohexanol.^f Methoxy cyclohexanol.

main peak at the chemical shift (δ) of approximately –114 ppm from the Si(OSi)₄ (Q⁴) species, along with a shoulder centered at –102 ppm from the Si(OSi)₃OH (Q³) entities. The Q⁴/Q³ ratio of TS-S-(0.05) and TS-C-(0.1), calculated from the deconvoluted peaks (dashed lines), was lower than that of the other TS-1 samples. The higher percentage of Q³ in the silanized samples indicated that the TS-1 aggregates had a more hydrophilic surface. Almost no Si(OSi)₂(OH)₂ (Q²) signals were observed in all the spectra. A second group of signals in the ²⁹Si MAS NMR spectra, corresponding to the CH₃(SiOSi)₃ (T³) moieties ($\delta \approx -68$ ppm), were invisible in the case of TS-S-(0.05) and TS-C-(0.1). This indicated that 1,8-bis(triethoxysilyl)octane was incorporated into the zeolite aggregates. Compared with TS-S-(0) (a) and TS-C-(0), the lower percentage of Q³ in the calcined TS-S-(0.05) and TS-C-(0.1) indicated that the TS-1 aggregates had a more hydrophobic surface, which was analogous to a previous report [47].

To investigate the catalytic capacity of the resulting hierarchical nanozeolite aggregates, epoxidation of alkenes (1-hexene and cyclohexene) with H₂O₂ as an oxidant was used as a probe reaction. As shown in Table 1, the TS-1 aggregate catalysts prepared in the presence of 1,8-bis(triethoxysilyl)octane showed similar activity with the reference samples TS-S-(0) and TS-C-(0) in the epoxidation of 1-hexene. These results agreed with those reported by Schmidt *et al.* [48,49], where the mesoporous TS-1 and conventional TS-1 showed similar activity for the epoxidation of 1-octene. The reason for this was that the small 1-hexene molecules could easily diffuse into the channel of the MFI-type materials and were easily accessible to the active Ti site of the catalysts. Hence, the 1-hexene conversion mainly depended on the Ti content in the TS-1 zeolite. Correspondingly, the efficiency of H₂O₂ was similar for these samples.

The epoxidation of cyclohexene, a relatively large and bulky substrate, was further used to evaluate the catalytic activities of these silanized TS-1 samples. Surprisingly, these silanized TS-1 samples showed higher activity and epoxide selectivity than did the reference samples TS-S-(0) and TS-C-(0). The conversion of cyclohexene over the TS-S-(0.05) sample reached 6.2%, with 43% of epoxide selectivity, which was almost twice that of the reference nanocrystal TS-1 zeolite. Similarly, the mesopo-

rous TS-1 prepared with the aid of an amphiphilic organosilane with a single long alkyl moiety showed a conversion of about 5.9% for cyclohexene [47]. The small particle diameter and enhanced hydrophobic properties of TS-1 by surface modification with 1,8-bis(triethoxysilyl)octane provided easy access to the active Ti (IV) sites and showed a significant improvement in the catalytic activity for the epoxidation reaction. Most importantly, the TS-1 aggregates could curtail the filtration difficulties in the catalytic reaction to some extent.

4. Conclusions

A relatively simple and effective method was developed to synthesize hierarchical TS-1 zeolite aggregates based on the crystallization of seeds silanized by bridged organosilanes. These hierarchical materials not only preserved the advantages of the TS-1 nanoparticles and enhanced hydrophobicity but also allowed for easy recovery during the preparation of the zeolite and catalytic applications due to the large aggregates. All these features positively influenced their catalytic properties for alkene epoxidation with hydroperoxides. Most importantly, this silanization method could also be used to assemble other nanozeolites with different topologies into large aggregates, which will well preserve the advantages of the nanoparticles and prevent difficulties in recovery and reuse.

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Graphical Abstract

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As-synthesized zeolitic seeds/nanocrystallites were assembled to nanocrystal aggregates by bridged organosilanes under hydrothermal conditions, where the bridged organosilane covered the surface of the seeds/crystallites with two condensable heads. These TS-1 zeolite aggregates possessed both the properties of the conventional nanoparticle of TS-1 zeolites and variable surface features, which enhanced the catalytic properties of hydroperoxides for alkene epoxidation.

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桥联有机硅烷组装多级孔TS-1聚集体及其催化性能研究

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摘要: TS-1分子筛在 H_2O_2 参与的有机物分子选择氧化及环氧化反应中具有优异的催化性能, 一直广受关注. 目前, 随着精细化工反应中大分子及液相反应的增多, 目前工业上使用的微米级尺寸的沸石晶粒催化材料因其狭窄的孔道和较大的扩散阻力而越来越不能满足工业的实际生产需求与应用. 小晶粒纳米沸石由于具有较大的外比表面积和较高的晶内扩散速率, 因而在提高催化剂的利用率、增强大分子转化能力、减小深度反应、提高选择性以及降低结焦失活等方面均表现出优越的性能. 然而, 尺寸低于100 nm的沸石又存在着分离问题. 因此, 具有高催化活性、又能一步实现分离与回收的纳米沸石聚集体的合成, 引起了人们的研究兴趣. 目前可以通过使用聚苯乙烯球、球形阴离子交换树脂、硅烷化聚合物、聚合诱导胶体聚集(PICA)等实现纳米沸石聚集体材料的合成. 其中采用有机硅烷化试剂来制备多级孔纳米沸石聚集体材料提供了一种新的路线. 在沸石晶体表面修饰上有机硅烷化试剂, 含Si-C键的有机硅烷化物种可以有效地阻止沸石颗粒的晶体生长, 抑制形成大的沸石晶体, 从而得到纳米粒子聚集体; 同时有机硅烷化物种也对纳米沸石进行了表面改性, 提高了其疏水性. 特别是在有机相中硅烷化沸石可以形成小的、均匀的、聚集的疏水性的纳米沸石. 同时, 硅烷化试剂的本质和分子大小是沸石聚集体中多级孔大小的决定性因素. 具有可调结构的多级孔沸石晶体可以通过在常规的碱性沸石合成混合物溶液中添加一个两性有机硅表面活性剂而合成. 研究发现, 固定在沸石纳米晶表面的有机硅烷物种Si-C键能部分抑制纳米颗粒进一步聚集成较大的晶体, 使用硅烷化晶种的方法可以合成具有高比表面的多级孔ZSM-5等沸石. 然而, 目前已报道的通过硅烷化晶种方法中得到的多级孔TS-1沸石材料的尺寸仅有100–150 nm, 仍不利于分离和回收. 近来桥联有机硅烷试剂进入人们的视野——通过干胶法合成多级孔 β 沸石, 然而它们的尺寸也只有300–500 nm, 反应分离和回收仍然非常困难.

本文采用有机桥联硅烷化合物作为硅烷化试剂, 将TS-1纳米沸石晶种或者晶体组装聚集成大的沸石聚集体. TEM和SEM结果表明, 桥联有机硅烷在沸石晶体的聚集和后续的晶体生长中起到了非常有效的作用, 成功地将100 nm左右的纳米沸石晶种或晶体桥联/组装成宏观大尺寸(5–40 μm)的沸石聚集体. 这些TS-1聚集体具有较好的机械强度, 即使连续超声1 h也不会毁坏其结构, 表明所得到的沸石材料可以在制备上解决分离困难并且在催化应用上容易回收. XRD, BET以及UV-Vis分析结果表明, 引入在TS-1沸石晶种或者晶体溶液中有有机硅烷试剂不会影响沸石的晶体结构、微孔体积以及Ti的配位状态. 将 H_2O_2 作为氧化剂评价TS-1沸石聚集体和传统的纳米TS-1在烯烃环氧化反应中的催化性能, 结果表明, 硅烷化步骤对小分子己烯氧化的活性和选择性的影响不大, 在环己烯大分子的氧化反应里表现出了较高的活性和选择性.

关键词: 桥联有机硅烷; TS-1沸石晶种; TS-1沸石晶体; 沸石聚集体; 烯烃环氧化反应

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