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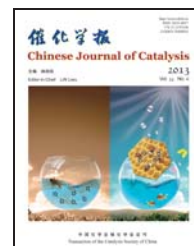
Article

Synthesis and catalytic oxidation performance of Al–TS-1

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A R T I C L E   I N F O

A B S T R A C T

The preparation of titanium silicalite-1 (TS-1) containing Al (Al-TS-1) and its catalytic oxidation properties were investigated systematically. The features of Al-TS-1 were characterized using X-ray diffraction, ultraviolet-visible spectroscopy, inductively coupled plasma atomic emission spectroscopy, ^{27}Al magic-angle spinning and ^{29}Si magic-angle spinning nuclear magnetic resonance spectroscopies, and scanning electron microscopy. The results showed that incorporation of Al into the TS-1 framework influences the amount of framework Ti in Al-TS-1. However, when the Al/Si ratio is lower than 0.005, the amount of framework Ti in Al-TS-1 is hardly affected. Neither the Al centers nor the Ti centers in the Al-TS-1 framework influence the acidic catalytic and catalytic oxidation performance. Al in the Al–TS-1 framework suppressed desilication of silica species adjacent to framework Ti species in Al–TS-1 in a basic catalytic system, so Ti active sites in the Al–TS-1 framework could be protected.

1. Introduction

Titanium silicalite-1 (TS-1) is obtained by partial isomorphous substitution of Si in S-1. Since it was first reported in 1983 [1], it has been widely used in various organic catalytic processes using hydrogen peroxide as a mild oxidant [2–4]. It has been reported that the catalytic activity of TS-1 is attributable to the framework Ti species in the TS-1/H_2O_2 system. The framework tetrahedral Ti^{4+} ions interact with H_2O_2 to form active intermediates, and then active oxygen is transferred to the substrate to form the corresponding oxide [2,3,5–7]. The physicochemical properties of TS-1 such as the coordination states of Ti species, surface acidity, hydrophobicity, and incorporation of heteroatoms into the TS-1 framework play a crucial role in its catalytic properties. Recently, many heteroatoms such as Al, B, and Fe have been incorporated into the TS-1

framework to form bifunctional catalysts [8–12]. In particular, Al-TS-1, with Al incorporated into the TS-1 framework, which has Brönsted acid sites, is a promising and excellent catalyst for the bifunctional catalysis of acidic reactions/oxidations such as alcohol etherification reactions [13–15]. However, the presence of Brönsted acid sites could result in side reactions of the oxide in the oxidation reaction [16–19].

It is worth noting that the main interest is the effect of framework Al and Ti atoms in the Al-TS-1 zeolite on the catalytic properties. Thangaraj et al. [9] reported that the low acitvity in hydroxylation reactions was related to decomposition of H_2O_2 as a result of the presence of Al in Al-TS-1, but it exhibited similar activity to that of ZSM-5 in *m*-xylene isomerization reactions. It is concluded that Ti in Al-TS-1 does not influence the acid catalytic properties, but the presence of Al decreases its catalytic performance in oxidation reactions.

Ovejero et al. [15] thought that the catalytic oxidation activity increased because the presence of Al changed the surface hydrophobicity when the Al/Si ratio in Al-TS-1 was 0.70. It is therefore not clear whether the framework Al influences the catalytic oxidation of framework Ti. We have therefore studied the synthesis of Al-TS-1, and performed a detailed study of the physicochemical properties and catalytic oxidation performance of Al-TS-1. The study showed that the framework Al species in Al-TS-1 have no influence on the catalytic oxidation properties originating from framework Ti, and vice versa. It was also found that the presence of Al inhibits desilication adjacent to framework Ti species in the ammoximation of cyclohexanone catalyzed by Al-TS-1. In addition, our study may provide information for designing highly stable TS-1 zeolites in basic reaction systems.

2. Experimental

2.1. Preparation and characterization of Al-TS-1

Al-TS-1 samples with different Al contents were synthesized using a hydrothermal method [20,21]. First, a specific amount of aluminum isopropoxide [AIP, analytical reagent (AR) grade; Sinopharm Chemical Reagent Co., Ltd.] was added to tetrapropylammonium hydroxide (TPAOH, 25 wt%, industrial product) aqueous solution. This was followed by the slow addition of a mixture of tetraethoxysilane (TEOS, AR; Sinopharm Chemical Reagent Co., Ltd.) and tetrabutyl titanate (TBOT, AR; Shanghai LingFeng Chemical Reagent Co., Ltd.). The resulting mixture was crystallized at 170 °C for 48 h after hydrolyzing and removing the alcohol. The product was separated by filtration, washed with distilled water, dried overnight, and calcined. The molar ratios of the raw materials were TEOS:TBOT:AIP:TPAOH:H_2O = 1:0.0167:(0.001–0.0167):0.18:18.

Synthesis of TS-1: except for the addition of AIP, the procedure was the same as that for Al-TS-1.

The crystalline phase was determined using X-ray diffraction (XRD; Bruker D8 ADVANCE; Cu K$_\alpha$ radiation, scanned area 2θ = 5°–35°). The Ti coordination states of the catalysts were investigated using ultraviolet-visible (UV-Vis) spectroscopy (Shimadzu UV-2550, $BaSO_4$ as the reference). The Al and Si coordination states of the catalysts were determined using magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy. The Ti and Al contents were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo IR ISIntrepid II). The morphologies and sizes of the crystallites were determined using high-resolution field-emission scanning electron microscopy (SEM; Hitachi S-4800).

2.2. Epoxidation of 1-hexene

The liquid-phase epoxidation of 1-hexene with H_2O_2 was carried out at 60 °C for 2 h, with stirring, in a batch reactor consisting of a round-bottomed flask (50 ml) equipped with a condenser. The reaction mixture was as follows: 0.05 g of catalyst, 10 ml of methanol as solvent, 10 mmol of 1-hexene, and 10

mmol of H_2O_2 (~30 wt% aqueous solution) as the oxidant. The product was analyzed using gas chromatography (GC; Agilent GC7890A gas chromatograph equipped with a 30 m × 320 μm × 0.25 μm DB-WAX capillary column). The amount of unconverted H_2O_2 was determined by titrating with 0.05 mol/L $Ce(SO_4)_2$ aqueous solution.

2.3. Ammoximation of cyclohexanone

The liquid-phase ammoximation of cyclohexanone was conducted in a similar manner, except that the H_2O_2 was added within 90 min at a constant speed. The reaction conditions were as follows: 75 °C, 2 h, 0.45 g of catalyst, 10 ml of *tert*-butyl alcohol aqueous solution (*tert*-butyl alcohol, AR, 85 wt%) as solvent, 30 mmol of cyclohexanone (AR), 51 mmol of $NH_3 \cdot H_2O$ (AR, 25 wt%), and 33 mmol of H_2O_2 (~30 wt% aqueous solution). The product was analyzed on an Agilent GC7890A GC equipped with a 30 m × 320 μm × 0.25 μm DB-WAX capillary column.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. XRD

Figure 1 shows the XRD patterns of Al-TS-1 with different Al/Si ratios. All the samples exhibit the typical diffraction peaks of an MFI-type structure. The relative crystallinities of all the Al-TS-1 samples are almost the same, so incorporation of Al into TS-1 has no influence on the crystallization of Al-TS-1 [14].

3.1.2. UV-Vis spectra

The Ti coordination state of Al-TS-1 was investigated using UV-Vis spectroscopy (Fig. 2). The bands at 210, 260, and 330 nm demonstrate that the Ti atoms exist in a tetrahedral coordination in the zeolitic framework, octahedral Ti species, and anatase, respectively [22]. There is a strong band at 210 nm for all the Al-TS-1 samples, in accordance with the literature [11,15]. It is worth noting that the peak intensity at 210 nm of
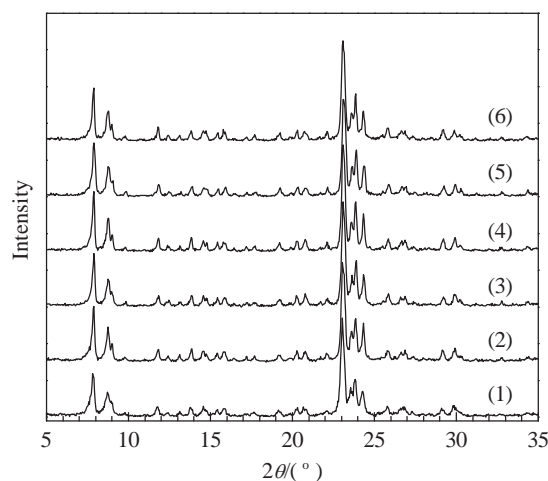
Fig. 1. XRD patterns of Al-TS-1 with different Al/Si ratios. (1) 0.0167; (2) 0.01; (3) 0.005; (4) 0.002; (5) 0.001; (6) 0.
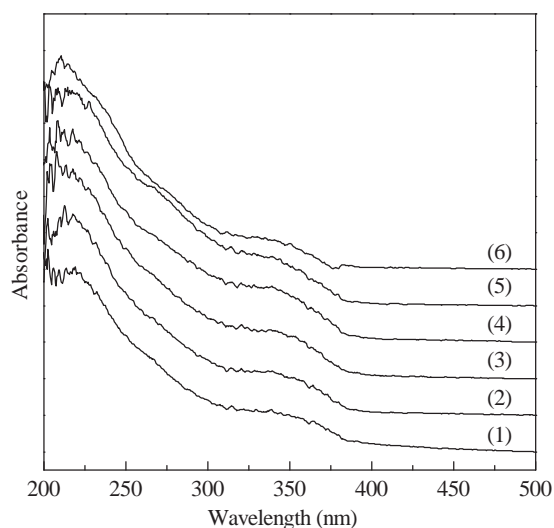
Fig. 2. UV-Vis spectra of Al-TS-1 (Si/Ti = 60) with different Al/Si ratios. (1) 0.0167; (2) 0.01; (3) 0.005; (4) 0.002; (5) 0.001; (6) 0.

Fig. 3. Ti/Si and Al/Ti ratios of Al-TS-1(Si/Ti = 60) synthesized with different Al/Si ratios.

Al-TS-1 with Al/Si > 0.005 is lower than that of Al-TS-1 with Al/Si ≤ 0.005, even in normal TS-1 (Si/Ti = 60) samples; that is, the amount of framework Ti species in Al-TS-1 is related to the amount of framework Al species in Al-TS-1. In addition, anatase was found both in Al-TS-1 and TS-1 samples, and they also have the similar peak pattern. Consequently, we can conclude that the incorporation of Al into Al-TS-1 does not affect the distribution of framework Ti species in Al-TS-1.

3.1.3. ICP-AES

Figure 3 shows the Ti/Si and Al/Si ratios of Al-TS-1 synthesized with different Al/Si ratios, and same Si/Ti ratios (Si/Ti = 60 in raw material) measured by ICP-AES. The results indicate that the Ti/Si ratio in Al-TS-1 is nearly the same as that in normal TS-1 when the Al/Si ratio is lower than 0.005, i.e., Al hardly influences the insertion of Ti into Al-TS-1. When the Al/Si ratio is higher than 0.005, the Ti/Si ratio decreases with increasing Al content, which shows that the insertion of Al inhibits Ti in-
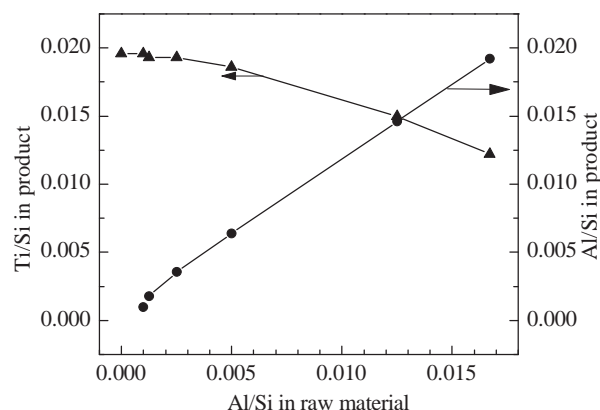
sertion into the zeolitic framework. However, the Al/Si ratio increases linearly with increasing Al content because incorporation of Al into the MFI-type framework is easier than insertion of Ti. During the synthesis of Al-TS-1 at high Al contents, Al and Ti atoms compete for insertion into the Al-TS-1 framework. Too much framework Al species may prohibit incorporation of Ti into the Al-TS-1 framework, thus the Ti/Si ratio of Al-TS-1 is lower, as shown by the UV-Vis results [11,15].

3.1.4. SEM

Figure 4 shows the SEM images of Al-TS-1 (Si/Ti = 60) synthesized with different Al/Si ratios. All the Al-TS-1 samples have an ellipsoid morphology similar to that of TS-1, but the particle size of Al-TS-1 is much larger than that of normal TS-1, The particle size of Al-TS-1 increases with the increase of Al. It is worth noting that the morphology of Al-TS-1 undergoes a significant change. The morphology of Al-TS-1 presents obvious agglomeration of small particles at high Al content, which shows that the presence of Al in the synthesis is beneficial to the formation of nuclei. These results are in agreement with those of Melero et al. [14] and Serrano et al. [23] regarding the effect of Al atoms on crystallization.
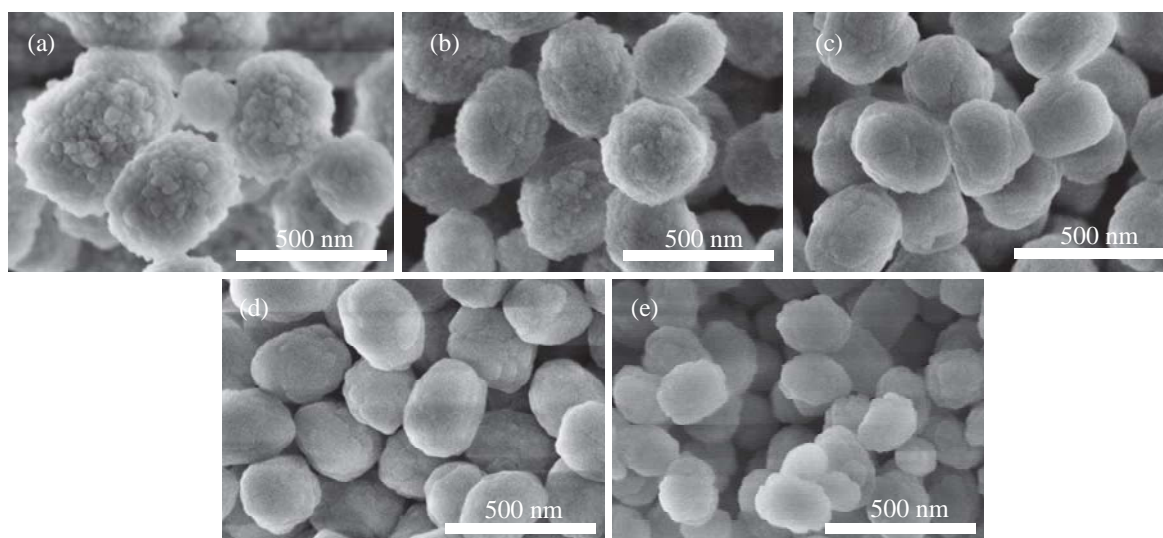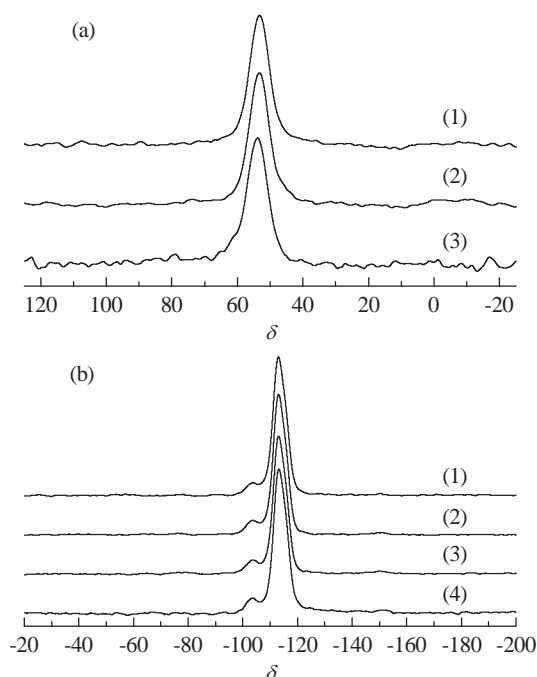

Fig. 4. SEM images of Al-TS-1 (Si/Ti = 60) synthesized with different Al/Si ratios. (a) 0.0167; (b) 0.01; (c) 0.0025; (d) 0.001; (e) 0.

Fig. 5. ^{27}Al MAS NMR (a) and ^{29}Si MAS NMR (b) spectra of Al-TS-1 (Si/Ti = 60) synthesized with different Al/Si ratios. (1) 0.0167; (2) 0.002; (3) 0.001; (4) 0.

3.1.5. ^{27}Al and ^{29}Si MAS NMR

Figure 5(a) shows the ^{27}Al MAS NMR spectra of Al-TS-1 (Si/Ti = 60) synthesized with different Al/Si ratios. Normally, the signal at δ = 50 is associated with Al atoms in tetrahedral environments in the framework, and the signal at δ = 0 is assigned to extra-framework Al species [15]. Figure 5(a) shows that all the Al-TS-1 samples have a similar tetrahedral coordination state belonging to Al in the framework; that is, Al atoms can be inserted into Al-TS-1 framework more easily than Ti atoms can [11,15]; this is in good agreement with the ICP-AES results. The ^{29}Si MAS NMR spectra of Al-TS-1 (Si/Ti = 60) samples synthesized with different Al/Si ratios and normal synthesized TS-1 (Si/Ti = 60) are depicted in Figure 5(b). The spectra clearly exhibits two broad features associated with Q^3 (δ = −95.0 to −104.0) and Q^4 (δ = −104.0 to −115.0). The peaks in the Q^3 region arise from a silanol group with three T–O–T (T is Ti or Si) groups, and those in the Q^4 region are attributed to Si connected to four T atoms by O atoms. Therefore, Si species in Al-TS-1 and TS-1 exist mainly in the form of Q^4 state. Furthermore, the amount of Al in Al-TS-1 is hardly related to the coordination state of Si in the framework. Al-TS-1 samples with different Al contents have similar hydrophobicities with TS-1 when they have the same Ti contents by analyzing Q^3 form.

3.2. Catalytic activity of Al–TS-1

3.2.1. Epoxidation of 1-hexene

Figure 6 shows the catalytic oxidation performances of Al-TS-1 samples synthesized with different Al/Si ratios in the epoxidation of 1-hexene. Besides 1,2-epoxyhexane, the final products also include the alcohol ether produced by acid catalysis with the solvent. However, we did not detect
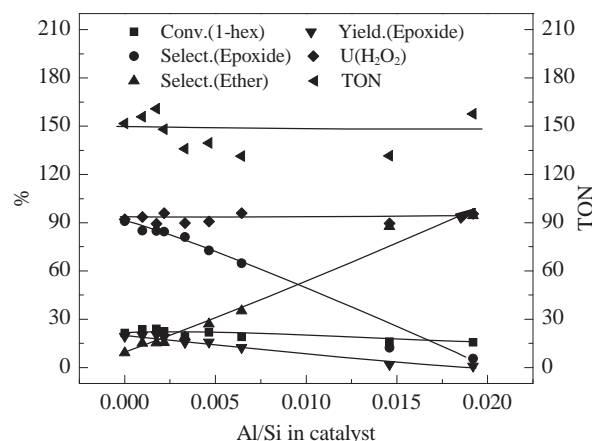
Fig. 6. Catalytic oxidation performance of Al-TS-1 synthesized with different Al/Si ratios in epoxidation of 1-hexene.

1,2-hexanediol, which is the product of 1,2-epoxyhexane reacted with H$_2$O in the existence of acid site. We consider that alcoholysis can proceed more easily than hydrolysis [16,24].

It can be demonstrated that the conversion of 1-hexene for all the samples was nearly invariant when Al/Si ≤ 0.005. However, the conversion of 1-hexene decreased slightly with increasing Al content in Al-TS-1 when the Al/Si ratio was higher than 0.005. This is because there are relatively small numbers of Ti species in Al-rich Al-TS-1. However, the turnover numbers (TON) of 1-hexene obtained over all the samples were high in each case, as well as the effective use of H$_2$O$_2$. This shows that the presence of Al in the framework does not influence the catalytic oxidation performance catalyzed by Ti active sites. Li et al. [19] have studied the effect of Al impurities on the epoxidation of propylene with TS-1. If a small amount of base is added to the TS-1 framework, side reactions can be inhibited and the propylene epoxide selectivity increases significantly. Therefore, although Al atoms have an effect on the incorporation of Ti into Al-TS-1 when the Al content exceeds a certain amount, framework Al species do not influence the catalytic oxidation performance originated by the Ti active sites. This is different from some of the results reported in the literature [9,15]. Thangaraj et al. [9], thought that Al species lead to decomposition of H$_2$O$_2$. However, the real reason may be that the amounts of extra-framework Ti species resulted in decomposition of H$_2$O$_2$. This is because Ti species cannot totally insert into the framework, and some extra-framework Ti species are present when Si/Ti = 24 and Si/Al = 45. However, Ovejero et al [15], believed that the presence of Al in Al-TS-1 samples modifies the activity for oxidation compared with that in TS-1, with an optimum Al/Ti molar ratio of ca. 0.7; this seems to be related to changes in the hydrophilic/hydrophobic characters of the samples. However, we can conclude that Al-TS-1 with various Al contents and TS-1 have similar hydrophilic/hydrophobic characters from the results in Fig. 5(b), so the catalytic oxidation performance cannot be influenced greatly. The framework Al species therefore do not affect the catalytic oxidation performances of Ti centers in catalytic oxidation using Al-TS-1.

For the acid catalysis of Al-TS-1, originating from Al in the framework, the selectivity for the alcohol ether increased with
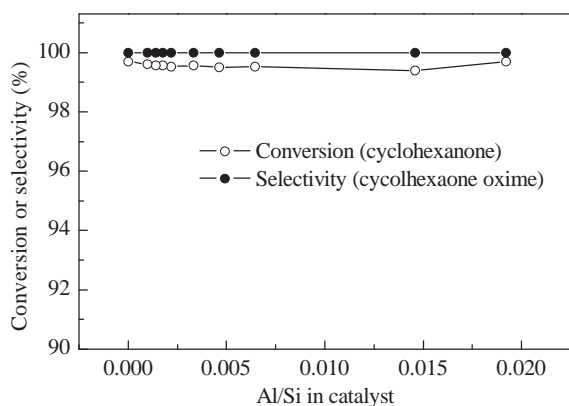
Fig. 7. Catalytic oxidation performances of Al-TS-1 synthesized with different Al/Si ratios in ammoximation of cyclohexanone.

increasing Al content, whereas the selectivity of 1,2-epoxyhexane decreased. This shows that the presence of Ti in Al-TS-1 has no influence on its acidic catalytic performance, which is in accord with a previous report [9].

3.2.2.   Ammoximation of cyclohexanone catalyzed by Al-TS-1

3.2.2.1.   Initial activity

Figure 7 shows the catalytic properties of Al-TS-1 synthesized with different Al/Si ratios in the ammoximation of cyclohexanone. The conversion of cyclohexanone and the selectivity for cyclohexanone oxime are the same for all the Al-TS-1 samples. This shows that incorporation of Al into the TS-1 framework has no influence on the catalytic properties catalyzed by Ti active sites. This has the same conclusion as that reached for epoxidation of 1-hexene. This is because excess NH_3 in the liquid system neutralizes the Brönsted acid sites originating from framework Al species [19], so the catalytic oxidation performance of Al-TS-1 stays well.

3.2.2.2.   Reusability of Al-TS-1 for ammoximation of cyclohexanone

Figure 8 shows the reusability of Al–TS-1 in the ammoximation of cyclohexanone when Si/Al = 100 and Si/Ti = 60. Al-TS-1
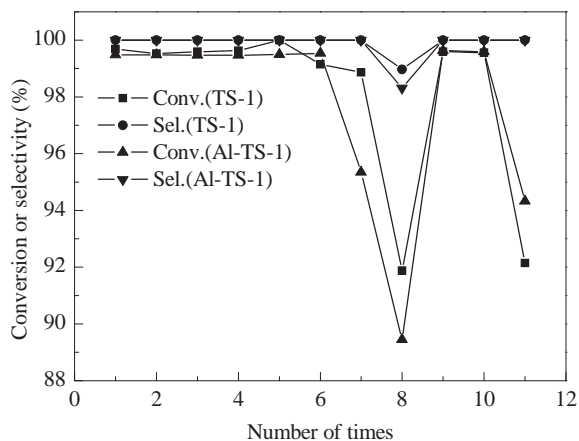

Fig. 8. Reusability of Al-TS-1 in ammoximation of cyclohexanone.
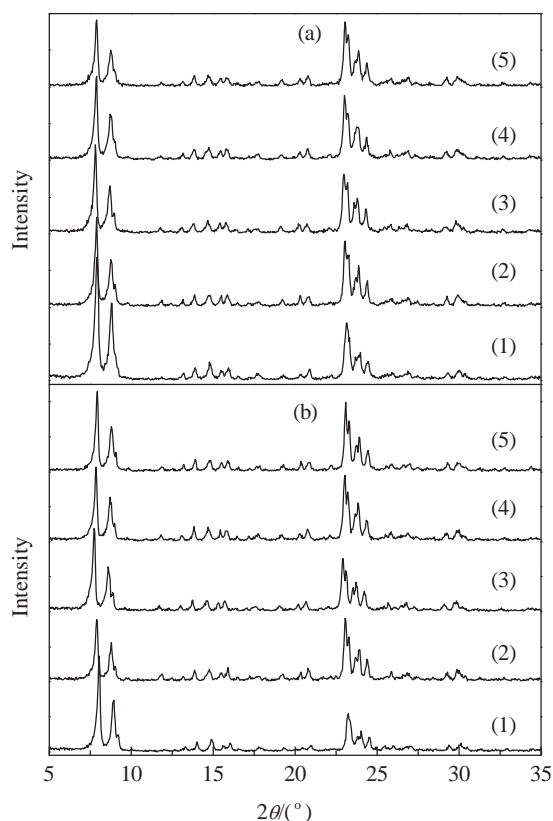

Fig. 9. XRD patterns of Al-TS-1 (a) and TS-1 (b) reused in ammoximation of cyclohexanone. (1) Fresh; (2) First; (3) Third; (4) Sixth; (5) Deactivated.

Table 1
Changes in Si/Ti and Si/Al ratios in reused TS-1 and Al-TS-1 measured by ICP.

Sample	Si/Ti	Si/Al
TS-1	51.1	—
TS-1-resued	52.1	—
Al-TS-1	59.9	86.3
Al-TS-1-used	59.4	81.6

and TS-1 (Si/Ti = 60) have highly catalytic oxidation performances. After being reused eight times, the activities of all the samples decreased, but the activity of the deactivated catalyst can be recovered to the initial activity by calcining at 550 °C.

To analyze changes in structure of Al-TS-1 and TS-1 for ammoximation of cyclohexanone thoroughly, XRD and ICP-AES measurements were performed on Al-TS-1 and TS-1 showed in Fig. 9 and Table 1.

The XRD patterns of Al-TS-1 and TS-1 reused in the ammoximation of cyclohexanone are shown in Fig. 9. Both Al-TS-1 and TS-1 kept excellent MFI structures after being reused. Table 1 shows that the Si/Ti ratio of TS-1 increased from 51.1 to 52.1 after reuse, which showed that the rate of desilication was slower than that of Ti removal originated by desilication [25,26]. However, the Si/Ti ratio in Al-TS-1 varied from 59.9 to 59.4. This indicates that Ti removal during reuse was suppressed to some degree. In contrast, the Si/Al ratio of Al-TS-1 after reuse decreased from 86.3 to 81.6. This means that desil-

Table 2
Si/Ti and Si/Al ratios of different catalysts treated with NaOH measured by ICP.

Sample	Si/Ti (Untreated)	Si/Al (Untreated)	Si/Ti (Treated)	Si/Al (Treated)
TS-1	54.9	—	52.3	—
ZSM-5	—	55.8	—	52.1
Al-TS-1	79.9	55.9	79.8	52.1

Treatment conditions: 1 g of zeolite dissolved in 30 ml of NaOH aqueous solution (0.2 mol/L) at 65 °C for 0.5 h.

ication is much more extensive than dealumination originating from extraction of Si species. The Si species adjacent to Al in the Al-TS-1 framework are therefore more easily attacked by alkaline molecules than the Si species neighboring to Ti, and this favors retention of the tetrahedral coordination state of Ti in the zeolitic framework.

3.2.2.3. Dissolution rule of Si and Ti

To confirm the rule for dissolution by alkali, TS-1, ZSM-5, and Al-TS-1 [27] were treated with NaOH aqueous solution. The changes of Si/Ti and Si/Al ratios were analyzed using ICP-AES. The results are shown in Table 2. The Si/Ti ratio in TS-1 decreased from 54.9 to 52.3, and the Si/Al ratio in ZSM-5 decreased from 55.8 to 52.1. This shows that desilication is even easier in ZSM-5 than it is in TS-1. However, for the Al-TS-1 samples, the Si/Ti ratio was almost constant after treatment with alkali, whereas the Si/Al ratio decreased from 55.9 to 52.1. We can see that the rule for extracting Si in Al-TS-1 is the same as that in ZSM-5. This clearly demonstrates that the presence of framework Al in Al-TS-1 inhibited desilication next to framework Ti species, and protected Ti from losing its tetrahedral state.

4. Conclusions

Al atoms can be incorporated into an MFI framework more easily than Ti atoms can in the process of doping Al heteroatoms into the TS-1 framework. When the Al content in the starting material is higher than 0.005, it will greatly influence the formation of framework Ti species. However, when the Al/Si ratio is lower than 0.005, the presence of Al does not influence insertion of Ti into the zeolitic framework and oxida-

tion performance catalyzed by tetrahedral-state Ti species. Brönsted acid sites originating from framework Al species in Al-TS-1 can catalyze side reactions of 1,2-epoxyhexane with the methanol solvent in epoxidation of 1-hexene, but the presence of framework Ti species has no influence on the acid catalytic properties of framework Al species. In the ammoximation of cyclohexanone, desilication adjacent to Ti in Al-TS-1 is much more difficult than it is in TS-1. This could be used in the design of high-performance catalysts for ammoximation of cyclohexanone.

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Graphical Abstract

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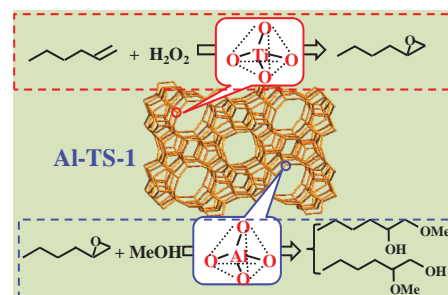
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Al-TS-1的合成及催化氧化性能

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摘要: 系统研究了Al掺杂TS-1 (Al-TS-1)分子筛的合成及其催化氧化性能, 采用X射线衍射、紫外-可见光谱、电感耦合等离子体发射光谱、扫描电镜、^{27}Al和^{29}Si固体核磁共振等手段对Al-TS-1样品进行了表征. 结果表明, 在合成过程中, Al的引入会影响TS-1中骨架Ti的形成, 但当Al含量低于一定值(Al/Si ≤ 0.005)时, 其影响很小. Al-TS-1中骨架Al和骨架Ti均不对其相应的酸催化和催化氧化作用产生影响. 骨架Al抑制了Al-TS-1在碱性应用体系中的与Ti相邻Si的溶脱, 从而保护了骨架Ti活性中心.

关键词: 铝掺杂TS-1分子筛; 合成; 氧化; 溶硅; 肟化

1. 前言

　　钛硅(TS-1)分子筛是纯硅沸石的同晶取代物, 自1983年首次合成以来[1], 广泛应用于以H_2O_2为氧化剂的绿色有机催化领域中[2~4]. 研究表明, TS-1/H_2O_2体系催化作用的基本历程是分子筛活性中心Ti首先活化H_2O_2形成活性氧物种, 然后活化氧有效传递到底物, 进而完成选择性氧化过程, 生成相应的氧化产物[2,3,5~7]. TS-1分子筛的结构特征, 如钛物种的配位状态、表面酸性和亲疏水性及杂原子引入等, 均会对其催化性能产生影响. 其中杂原子掺杂的TS-1分子筛引起了人们的广泛关注. 如将三价杂原子(如B, Al, Fe等)引入到TS-1分子筛骨架[8~12]可以得到双功能TS-1分子筛催化剂; 特别是将Al引入到TS-1分子筛骨架形成的Al-TS-1, 构建了Brönsted酸性位[13~15], 具有酸性/氧化性能的双功能催化特性, 在醇的醚化等反应中表现出很好的催化性能[11]. 诚然, 在非碱性反应体系中, Brönsted酸性位的存在会发生催化氧化的副反应[16~19].

　　实际上对于Al-TS-1分子筛, 研究者关注的深层次问题是, 骨架Al和骨架Ti是否会相互影响其各自的催化性能. Thangaraj等[9]研究表明, 由于Al的存在, 其分解H_2O_2造成了Al-TS-1催化苯羟基化反应活性降低, 但在

间二甲苯异构化反应中表现出与ZSM-5相似的催化性能. 这说明Ti的存在并未影响Al-TS-1的酸催化性能, 而Al的存在则降低了其催化氧化性能. Ovejero等[15]则认为, 当Al/Ti = 0.7时, 由于Al-TS-1表面亲疏水性的改变, Al的存在提高了Al-TS-1的催化氧化性能. 这说明该问题还未认识清楚, 特别是Al-TS-1中骨架Al对骨架Ti的催化氧化性能究竟是否有影响的问题. 因此, 本文在系统研究Al-TS-1分子筛合成的基础上, 对其结构特征进行了详细表征, 并进一步研究其催化氧化性能. 研究表明, Al-TS-1分子筛中骨架Al的存在并没有影响骨架Ti的催化氧化性能, 反之亦然. 进一步对Al-TS-1分子筛应用于环己酮氨肟化反应的研究表明, Al的存在抑制了反应过程中由于与钛相邻硅的溶脱而造成的活性钛的流失. 这对于设计在碱性体系中应用的高稳定性的TS-1分子筛催化剂具有重要的指导意义.

2. 实验部分

2.1. Al-TS-1的制备和表征

　　采用水热法合成不同Al含量的Al-TS-1分子筛[20,21]. 将异丙醇铝(AIP, AR,国药集团化学试剂有限公司)溶解到模板剂四丙基氢氧化铵(TPAOH, w = 25%, 工业级产品)的稀溶液中, 并缓慢滴入一定配比的正硅酸四乙酯

(TEOS, AR, 国药集团化学试剂有限公司)和钛酸四丁酯(TBOT, AR, 上海凌峰化学试剂有限公司)的混合液, 经水解、赶醇, 于170 °C水热晶化48 h, 晶化产物抽滤、洗涤、烘干和焙烧后得到Al-TS-1催化剂. 分子筛合成物料摩尔配比为 TEOS:TBOT:AIP:TPAOH:H$_2$O = 1:0.0167:(0.001~0.0167):0.18:18.

TS-1 的合成, 除不添加 AIP 外, 所有步骤均同Al-TS-1.

采用 Bruker D8 ADVANCE 型 X 射线衍射 (XRD) 仪 (Cu K_α 射线, 扫描范围 2θ = 5°~35°) 测定晶相; 用Shimadzu UV-2550 型紫外-可见 (UV-Vis) 光谱仪 (BaSO$_4$为参照, 测试范围190~500 nm) 表征Ti的状态; 用固体魔角核磁共振谱 (MAS-NMR) 测定骨架Si、Al配位状态; 用Thermo IR ISIntrepidⅡ型电感耦合等离子体发射 (ICP)光谱仪测定Ti含量; 用Hitachi S-4800型冷场高分辨率发射扫描电子显微镜 (SEM) 测定颗粒大小.

2.2. 正己烯环氧化反应

以50 ml圆底烧瓶为反应容器, 并连接冷凝管作为冷凝装置, 60 °C水浴加热反应2 h. 体系组成为: 0.05 g分子筛、10 mmol正己烯(反应底物)、10 mmol H$_2$O$_2$ (~30 wt% 水溶液) 和10 ml甲醇(溶剂). 在Agilent GC7890A型气相色谱仪 (30 m × 320 μm × 0.25 μm DB-WAX毛细管柱) 上进行产物分析, 采用内标法 (环己酮为内标) 计算各组分的量, 从而得到反应物的转化率和产物的选择性. 反应体系中剩余的H$_2$O$_2$采用0.05 mol/L Ce(SO$_4$)$_2$溶液进行滴定.

2.3. 环己酮氨肟化反应

环己酮氨肟化反应在配有回流冷凝器和微量进样器的100 mL三颈烧瓶中进行. 将0.45 g催化剂, 30 mmol环己酮(AR), 51 mmol NH$_3$·H$_2$O (AR, 25%), 10 ml叔丁醇和水的混合溶剂(叔丁醇(AR)质量含量85 wt%), 一起加入到三颈烧瓶中, 并将33 mmol H$_2$O$_2$ (~30 wt% 水溶液)以匀速在90 min内滴加完毕, 反应温度75 °C, 磁力搅拌, 定时采样. 用Agilent GC7890A型气相色谱仪测定环己酮的转化率和环己酮肟的选择性.

3. 结果与讨论

3.1. Al-TS-1的合成与表征

3.1.1. XRD结果

图1为不同 Al/Si 比合成的 Al-TS-1 (Si/Ti = 60) 的XRD谱. 由图可知, 各Al-TS-1样品均具有典型的MFI结构特征峰, 且结晶度良好, 表明Al的引入并未改变TS-1的

MFI特征结构[14].

3.1.2. UV-Vis结果

图2为由不同Al/Si比合成的Al-TS-1 (Si/Ti = 60)的UV-Vis谱. 一般认为, λ = 210 nm附近出现的吸收峰归属于孤立的骨架Ti(IV)的特征峰; λ = 260 nm附近的对应于六配位非骨架钛的特征峰; λ = 330 nm附近的归属为锐钛矿物种的特征峰[22]. 由图2可知, 各Al-TS-1样品均在210 nm处有强吸收峰, 说明其均具有较好的骨架Ti(IV)分布, 与文献结果一致[11,15]. 但当Al/Si > 0.005时, 所合成的Al-TS-1分子筛在λ = 210 nm处的峰强度明显低于Al/Si≤0.005样品及常规TS-1的, 表明此时Al的存在在一定程度上影响了Ti进入分子筛骨架. 另外, Al-TS-1和TS-1均出现锐钛矿物种的特征峰, 且峰形相似, 说明Al的引入并未影响Ti的分布状态.

3.1.3. ICP结果

图 3 为当投料 Si/Ti = 60, 由不同 Al/Si 比合成的Al-TS-1分子筛经ICP测得的Ti/Si和Al/Si比值. 由图可知, 当Al/Si ≤ 0.005时, Al-TS-1的Ti/Si比基本维持与常规TS-1合成的水平, 即Al基本不影响Ti插入分子筛骨架; 当Al/Si > 0.005时, 其Ti/Si比则随着Al含量的增加而降低, 说明此时Al阻碍了Ti进入分子筛骨架. 而Al/Si比则呈现线性趋势, 说明Al几乎可以全部进入Al-TS-1分子筛骨架. 这是因为Al比Ti更容易进入MFI骨架. 若合成体系中Al含量过多时, Al会与Ti物种形成竞争关系, 抑制Ti物种进入分子筛骨架[11,15], 从而导致Ti/Si比降低, 与UV-Vis结果一致.

3.1.4. SEM结果

图4为由不同Al/Si比合成的Al-TS-1 (Si/Ti = 60)的SEM照片. 由图可知, Al-TS-1样品均为椭球形颗粒, 但颗粒尺寸均大于常规合成的TS-1分子筛, 且随着合成体系Al含量的增加而逐渐增大. 值得注意的是, 随着合成体系Al含量的增加, Al-TS-1呈现出明显小粒子堆积现象, 这说明Al在合成体系中有利于分子筛成核. 这和Melero等[14]和Serrano等[23]在研究Al-TS-1的晶化机理时提出的Al对晶化的影响一致.

3.1.5. ^{27}Al和^{29}Si MAS NMR谱

图5(a)为由不同Al/Si比合成的Al-TS-1 (Si/Ti = 60)的^{27}Al MAS NMR谱. 通常, δ = 50附近的吸收峰归属为四配位骨架Al, 而δ = 0附近的则对应于六配位的骨架外八面体Al物种[15]. 由图可知, 各Al-TS-1样品中均以四配位骨架Al形式存在. 这表明Al确实比Ti更容易进入骨架[11,15], 与ICP结果一致. 图5(b)为由不同Al/Si比合成的

Al-TS-1 (Si/Ti = 60)及TS-1的^{29}Si MAS NMR谱. 通常认为, δ = –104.0处的Q^3为Si连接一个羟基, 通过氧原子连接三个T原子的响应峰, δ = –115.0处的Q^4为Si通过氧原子连接四个T原子的响应峰. 可知, Al-TS-1和TS-1中Si均主要以Q^4形式存在, 且Al的存在及含量对骨架Si状态的影响很小. 从Q^3峰的分析可知, 不同Al含量、相同Ti含量的Al-TS-1与相同Ti含量的TS-1分子筛表面的亲疏水性基本相当.

3.2. Al-TS-1的催化氧化性能

3.2.1. 正己烯环氧化反应

图6为由不同Al/Si比合成的Al-TS-1 (Si/Ti = 60)催化正己烯环氧化反应结果. 由图可知, 反应产物中除了环氧化反应产物环氧己烷外, 还有酸催化的环氧己烷与溶剂的醇解反应产物醇醚, 但未检测到酸催化的水解产物1, 2-己二醇存在. 这可能是因为醇解反应比水解反应更易进行[16,24].

由图6可见, 当Al/Si ≤ 0.005时, Al-TS-1样品的正己烯转化率基本不变; 而当Al/Si > 0.005时, 正己烯转化率随着分子筛中Al含量的增加而稍有下降, 这是由于高Al含量Al-TS-1中活性中心Ti物种相对较少所致. 然而, 随Al含量的变化正己烯转化的TON值均较高; 同时, H_2O_2有效利用率也较高. 这说明Al-TS-1中骨架Al的存在并未影响骨架Ti活性中心的催化氧化性能. 李钢等[19]对TS-1中Al杂质对其催化丙烯环氧化性能的影响进行了研究, 发现, 只要碱中和了其中的酸性位, 环氧丙烷转化率就不受影响. 这说明尽管在合成过程中, 当Al含量较高时会影响Ti进入Al-TS-1分子筛骨架, 但骨架Al并未影响骨架Ti的催化氧化性能, 与文献[9,15]报道不同. Thangaraj等[9]认为, Al-TS-1中Al的存在导致了H_2O_2的分解, 而真实的原因可能是大量的非骨架Ti造成的. 因为在Si/Ti = 24, Si/Al = 45时, 如此高的Al含量, Ti不可能完全进入骨架, 因此一部分Ti是以非骨架形式存在. 而Ovejero等[15]认为, 当Al/Ti = 0.7时, 由于Al-TS-1表面亲疏水性的改变, 提高了它在Al-TS-1在烷烃氧化反应中的催化性能. 而由图5(b)可知, 不同骨架Al含量的Al-TS-1表面亲疏水性与TS-1分子筛基本相当, 它们的催化氧化性能差别也不大. 因此, 骨架Al不会明显影响Al-TS-1骨架Ti的催化氧化性能.

对于Al-TS-1的酸催化作用来说, 从醇解反应产物醇醚的选择性变化趋势可知, 其随着Al含量的增加而线性增加, 而环氧化产物的选择性的变化却线性下降. 这说明, Al-TS-1中骨架Ti的存在确实也没有影响其酸催化

性能, 与文献[9]报道一致.

3.2.2. 环己酮氨肟化反应

3.2.2.1. Al-TS-1的初始活性

图7为由不同Al/Si比合成的Al-TS-1 (Si/Ti = 60)催化环己酮氨肟化反应结果. 可知, Al含量对环己酮的转化率和环己酮肟的选择性基本无影响. 这说明在碱性催化体系中, Al引入TS-1骨架并不影响分子筛骨架Ti的催化氧化性能, 与Al-TS-1催化正己烯环氧化反应结果一致. 虽然Al的存在引入了Brönsted酸性位, 但体系中过量NH_3的存在中和了分子筛酸性位[19], 因而未对催化剂的催化氧化性能产生不利影响.

3.2.2.2. Al-TS-1的重复使用性

图8为Si/Al = 100, Si/Ti = 60合成的Al-TS-1上环己酮氨肟化反应的重复性能. 可知, Al-TS-1和TS-1 (Si/Ti = 60)表现出了相当的催化氧化性能. 重复使用8次后, 其活性降低. 失活催化剂经550 °C焙烧后, 其活性又恢复恢复到初始水平.

为了进一步分析Al-TS-1在环己酮氨肟化反应过程中结构的变化, 实验对Al-TS-1和TS-1在循环使用前后进行了XRD和ICP测试, 结果如图9和表1所示.

图9(a)和(b)分别为Al-TS-1和TS-1重复使用不同次数后的XRD谱. 可知, 在重复使用中Al-TS-1和TS-1均保持了完好MFI结构. 由表1可知, TS-1重复使用后, 其Si/Ti比从51.1升至52.1. 这说明反应过程中溶硅的速率小于源于溶Si而导致的Ti的脱除速率, 因而Si/Ti比升高[25,26]. 然而, Al-TS-1重复使用后, 其Si/Ti比从59.9降至59.4. 这表明Al-TS-1在重复使用过程中Ti的脱除有所抑制. 另外, Si/Al比从86.3降低至81.6, 意味着Al-TS-1在重复使用过程中溶硅的速率大于源于溶Si而导致的Al的脱除速率. 因此, 对于Al-TS-1而言, 在催化环己酮氨肟化反应过程中, 分子筛骨架中与Al相邻的Si比与Ti相邻的Si更容易受到碱的攻击而溶脱, 从而有利于钛硅分子筛骨架Ti的保持.

3.2.2.3. Si与Ti的脱出规律

为了进一步验证Al-TS-1的碱溶硅规律, 本文采用NaOH水溶液分别处理了TS-1, ZSM-5以及Al-TS-1[27], 并用ICP分析相应的Si/Ti比和Si/Al比在处理前后的变化, 结果示于表2. 可以看出, 经NaOH处理后, TS-1的Si/Ti比从54.9降至52.3, ZSM-5的Si/Al比从55.8降至52.1. 这说明在相同条件下, ZSM-5中的Si比TS-1中的更易受碱溶硅而脱除. 然而, Al-TS-1的Si/Ti比基本不变, 而Si/Al比从55.9降至52.1, 说明Si的脱除规律与ZSM-5的

一样. 这进一步表明, Al-TS-1中骨架Al的存在, 确实能够抑制与Ti相邻的Si的脱除, 从而保护了TS-1分子筛在使用过程中Ti的流失.

4. 结论

在TS-1骨架中引入杂原子Al的过程中, 由于Al更容易进入MFI分子筛骨架, 当Al/Si > 0.05才会影响骨架Ti的形成. 骨架Al的存在并未影响Al-TS-1分子筛表面亲水性和骨架Ti的催化氧化性能; 但因此而形成的Brönsted酸性位促进了烯烃氧化产物的开环反应; 同时, 骨架Ti的存在不影响骨架Al的酸催化反应性能. 在环己酮氨肟化反应中, Al-TS-1较TS-1具有更好的抑制与Ti相邻的Si的溶脱. 该结果对于设计高性能环己酮氨肟化催化剂具有一定的指导意义.