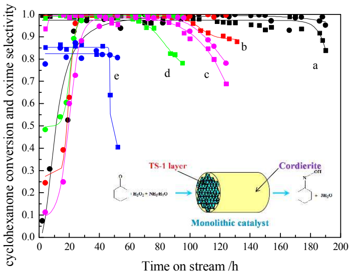
RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances



Catalytic performance of monolithic TS-1/cordierite catalysts for continuous heterogeneous cyclohexanone ammoximation reaction

Continuous Heterogeneous Cyclohexanone Ammoximation Reaction in Monolithic TS-1/Cordierite Catalyst

Libin Yang[a,b], Feng Xin[a]*, Junzhong Lin[a], Zhuang Zhuang[a], Rui Sun[a]

Abstract

In this study, hydrothermal synthesis was developed to prepare a thin titanium silicalite-1 catalyst layer in the internal channels of the honeycomb cordierite support, which was used for such a heterogeneous reaction in continuous operation. The as-prepared thin TS-1 catalyst layer was characterized by SEM, XRD, UV-vis and ATR-FTIR. Multiple hydrothermal syntheses were used for controlling crystalline growth to optimize the catalytic activity and lifetime. Besides, a monolithic TS-1/cordierite reactor with external looping was utilized to investigate the characteristics of continuously heterogeneous ammoximation reaction without organic solvent tert-butanol (TBA). The reaction results showed that the conversion of cyclohexanone and selectivity of oxime approached to more than 0.96 and 0.98, respectively. Meanwhile, compared with the reaction using TBA as solvent, the activity of monolithic TS-1/cordierite kept almost no change except for a longer lifetime.

Keywords:

Cyclohexanone ammoximation; Monolithic TS-1/Cordierite catalyst; Process intensification; Deactivation; Continuous operation

1. Introduction

The ammoximation of cyclohexanone had been demonstrated on industrial scale, and its product–cyclohexanone oxime, is an important intermediate for producing caprolactam (CPL) and Nylon 6 after the Beckmann rearrangement and polymerization. After the application of Titanium silicalite-1 (TS-1) catalysts, the challenges in ammoximation of cyclohexanone reaction, such as, multiple reaction steps, harmful oximation agents, and particularly, large amount of environmental polluted co-products have been solved.[1,2] Nevertheless, the usage of organic solvent tert-butanol (TBA) to intensify mass transfer has low poison to environment and increase the industrial cost. In addition, by-products generated in TBA can cause deactivation of TS-1 catalyst, because micropores in the catalyst can be blocked by these bulky organics.[3,4] Recently, the investigation into catalyst deactivation and liquid-solid separation in a slurry bed reactor for cyclohexanone ammoximation reaction had drawn considerable attention. Therefore, the solvent-free ammoximation reaction would be preferred. However, in case of remove solvent, the reactant mixture would be two phase and aqueous catalysis would be weakened due to the limitation of mass transfer in liquid-liquid two phase. Meanwhile， the maintain of conversion and selectivity is still very challenging.

TS-1 with MFI topology framework has drawn extensively attentions for its excellent catalytic oxidation performance[5-10] in H_2O_2 system at mild reaction condition, such as aromatic hydroxylation, alkene epoxidation, and ketone ammoximation. During the past decades, the investigations of TS-1 synthesis,[11,12] structural orientation preparation[13,14] and catalytic mechanism[15] have achieved significant progress. However, the utilization of direct cyclohexanone ammoximation in industrial plants has faced rather disappointed dilemma because the expensive

TS-1 catalyst powders would deactivate in a short lifetime and run off with the liquid products from a slurry bed reactor.

Herein, a solvent-free way with monolithic TS-1 as catalyst was chosen for cyclohexanone ammoximation reaction. The monolithic TS-1 catalyst, constructed by a support with many straight flow channels in parallel and a “flat” catalyst surface was prepared by directly multi-step hydrothermal syntheses. The activity of monolithic TS-1 catalyst applied continuously to a homemade structured reactor was evaluated in different reaction conditions. The catalytic performances of such a monolithic reactor characterized with low pressure drop, high-mass transfer rates, and easy scaling up,[2,16,17] in continuously heterogeneous cyclohexanone ammoximation reaction demonstrate a similar conversion and selectivity, and even a superior life time over a conventional fixed bed in large flow flux. We speculate it is because the channel size and catalyst layer thickness of the monolithic catalytic reactor are small enough to shorten the distance of mixing in bulk reactants and diffusing in the catalyst for multiphase catalytic reactions.

2. Experimental

2.1. Materials

The honeycomb cordierite supports (Jiangyin Huayin Porcelain & Machine Electricity Technology Co. Ltd., China) had parallel triangular channels with a length of about 90mm, width of 2, 1.5 and 1mm corresponding to 150, 250, 350 channels per square inch (cpsi), respectively. Tetrabutyl orthotitanate (TBOT, 98.5wt%, AR), tetraethyl orthosilicate (TEOS, 98wt%, AR), isopropanol (IPA, 98wt%, AR) and tetrapropyl ammonium hydroxide (TPAOH, 25wt%, AR) were purchased from Shanghai Aladdin Reagent Co., Ltd., China, and used as received. The reagents used in cyclohexanone ammoximation reaction were purchased from Tianjin Guang Fu Fine

Chemical Research Institute, China, including cyclohexanone (99wt%, AR), hydrogen peroxide (H_2O_2, 30wt%, AR), ammonia water ($NH_3 \cdot H_2O$, 25wt%, AR), cyclohexanone oxime (99wt%, AR), TBA (98wt%, AR), toluene (99.5wt%, AR), ethanol (99.7wt%, AR) and deionized water.

2.2. Preparation of monolithic TS-1/cordierite catalysts

The synthesis of TS-1 precursor was similar to the process described elsewhere.[11] Typically, a synthetic procedure for TS-1 precursor sol was as follows: 26.8g TEOS was dissolved into 30.5g TPAOH solution by a metric syringe pump in 30 min and hydrolyzed at 277K with 1 hour vigorous stirring. Then the mixture of 1.7g TBOT and 7.5ml anhydrous IPA was added slowly into the above-mentioned solution with the metric syringe pump in 1 hour. The resulted solution was further hydrolyzed at 277K for 1 hour. The removal of alcohol was maintained at 358K for 5 hours, and the volume loss of the hydrolyzed solution was compensated by adding deionized water. Finally, a transparent sol with molar composition of $1SiO_2$: $0.04TiO_2$: 0.3TPAOH: $25H_2O$ was obtained for coating on the internal surface of monolithic supports.

The monolithic cordierite supports were pretreated with deionized water in an ultrasonic bath to remove the contamination on the surface, and then calcined in air at 823K for 6 hours. The cleaned and dried support was submerged in an autoclave filled with the as prepared TS-1 precursor sol and sealed. The next step was a hydrothermal synthesis by fastening the autoclave with Teflon liner on a rotating bracket in an oven at 448K and 5 rpm for 3 days. By cooling down to the room temperature, the monolithic TS-1/cordierite catalyst was washed with deionized water, dried overnight at 383K, and calcined in air at a heating rate of 1K/min from room temperature to 823K and kept for 12 hours. The hydrothermal synthesis was repeated according to the same operation procedure in the autoclave filled with fresh TS-1 precursor and latest prepared monolithic TS-1/cordierite catalyst. The mass of TS-1 layer coated on monolithic cordierite was controlled by multiple hydrothermal syntheses. The solid powders settled on bottom of autoclave would be collected for comparing with the TS-1 layers on monolithic supports.

2.3. Characterizations of the prepared catalysts

The crystallite morphologic micrograph and energy-dispersive X-ray spectroscopic (EDS) analysis of the prepared catalysts were taken with a Hitachi S-4800 field emission scanning electron microscope (SEM) equipped with the Thermo Scientific energy dispersion X-ray fluorescence analyzer. XRD patterns were taken with Bruker D8 Focus using Cu Kα radiation in the 2θ angle range of 5-60° at 40 kV and 40 mA, and FT-IR spectra were recorded by Nicolet 6700 at the attenuated total reflectance (ATR) mode and transmission mode respectively. Besides, UV-visible measurements were performed on a Shimadzu UV-2550 using the diffuse reflectance mode with $BaSO_4$ as a reference.

2.4. Activity and lifetime of the as-prepared monolithic TS-1/cordierite catalysts

The catalytic ammoximation reaction of cyclohexanone was carried out continuously in a homemade glass reactor at nearly atmospheric pressure. As shown in Figure 1, the monolithic TS-1 catalyst was winded outside with Teflon tape and pushed into the reactor tightly. For a typical reaction using TBA as solvent, the reactor was fully filled with TBA before heating to a temperature range from 323 to 353K, and the liquid in the reactor was externally circulated through the monolithic TS-1/cordierite at controllable flow rate. Then, the mixture of ammonium hydroxide and TBA solution, cyclohexanone and H_2O_2 were fed into the reactor separately with three pumps. All the reactants kept at the constant feeding rates for molar ratio of cyclohexanone: H_2O_2: $NH_3{\cdot}H_2O$: TBA=1:1.2:1.5:10.

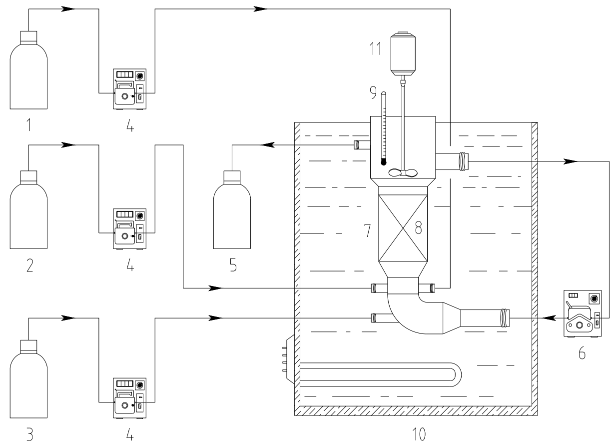


Fig. 1. Setup for continuous cyclohexanone ammoximation reaction in monolithic TS-1/cordierite catalyst

1 cyclohexanone tank; 2 hydrogen peroxide tank; 3 ammonia water (or mixture of ammonia water and t-butanol) tank; 4 constant flow pump; 5 reserve tank; 6 peristaltic pump; 7 reactor; 8 monolithic TS-1/cordierite catalyst; 9 thermometer; 10 water bath; 11 mechanical stirrer.

However, for the reaction in the absence of solvent TBA, the same volume of deionized water was filled into the reactor instead of TBA, and the feeding process was kept unchanged as presence of the solvent except for no feeding TBA. The samples sucked periodically were dissolved in ethanol and analyzed by SP3420 GC of, Beifen-Ruili Analytical Instrument Co. Ltd. The toluene was taken as an internal standard; flame ionization detector and a 30m of SE-54 capillary column were chosen. The start-up would last for approximately 40 hours before approaching to a continuous operation.

The conversion of cyclohexanone, the yield and the selectivity of oxime were defined respectively as follows:

The instantaneous conversion of cyclohexanone: $X_{CYC} = \frac{w_{CYC}^0 - w_{CYC}}{w_{CYC}^0}$ (1)

The yield of oxime: $Y_{oxime} = \frac{w_{oxime}}{w_{CYC}^0} \times \frac{98.15}{113.16}$ (2)

The selectivity of oxime: $S_{oxime} = \frac{Y_{oxime}}{X_{CYC}} = \frac{w_{oxime}}{w_{CYC}^0 - w_{CYC}} \times \frac{98.15}{113.16}$ (3)

w_{CYC}^0, w_{CYC} and w_{oxime} denote the initial, the instantaneous mass fraction of cyclohexanone, and the mass fraction of cyclohexanone oxime in reaction solution respectively.

The activity of the monolithic TS-1/cordierite catalysts was defined as

$$a = X_{CYC} / X_{CYC}^0 \quad (3)$$

Where, X_{CYC}^0 denote initially steady conversions of cyclohexanone.

The space velocity was calculated based on the mass of coated TS-1 catalyst as the following definition

$$WHSV = F_{all} / m_{TS-1} \quad (4)$$

Where, WHSV denotes the weight hourly space velocity; F_{all} is the feeding flow rate of all the components, g/h; m_{TS-1} is the mass of coated TS-1 layer on monolithic support, g.

3. Results and discussion

3.1. Characterization of Monolithic TS-1/cordierite catalyst

Firstly, the as-prepared monolithic TS-1/cordierite catalyst was investigated in detail. As schematically exhibited in Fig. 2, the catalyst contains a cordierite support and a layer of TS-1 on top. The cordierite support has a coarse inner surface of channels shown in Fig. 2a. After hydrothermal synthesis, a thin layer of TS-1 is deposited on the inner surface (Fig. 2b and c). From cross-sectional view in Fig. 2b, the thickness of the TS-1 crystal layer is about 3 μm after one-step crystallization. To increase the amount of TS-1 catalyst, multiple crystallizations which could generate thicker TS-1 layer were performed. In Fig. 2d, the thickness reaches 5 μm after two-step crystallizations. The TS-1 crystal size is about 100 nm as revealed in Fig. 2f. As shown in

Fig. 2c and Fig. 2e, the coarse surface was gradually smoothed through multiple crystallizations.

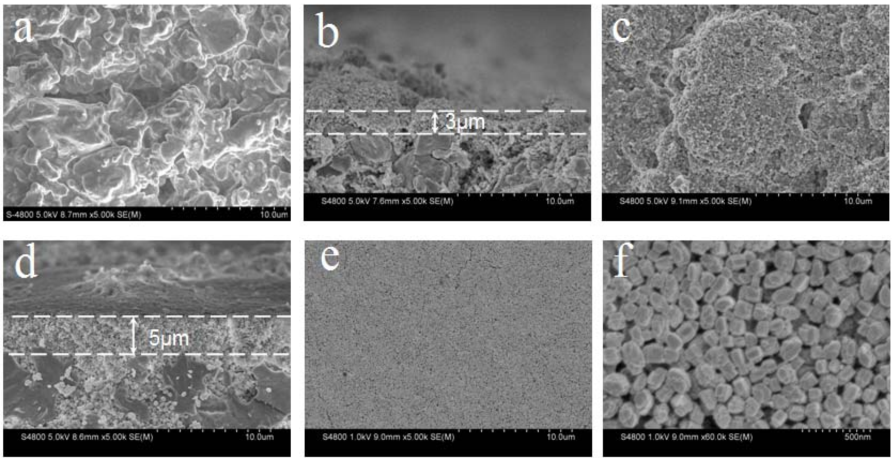


Fig. 2. SEM images of the monolithic TS-1/cordierite catalyst

(a) Top view of cordierite support; (b) cross-sectional and (c) top view of the TS-1 layers and cordierite support after one-step hydrothermal synthesis; (d) cross-sectional, (e) small and (f) big magnified top view of TS-1 layer and cordierite support after two-step hydrothermal syntheses

The growth speed of TS-1 layer was also investigated. The thickness and weight of TS-1 layer can be controlled by the step numbers of crystallization (displayed in Fig. S1). In the hydrothermal process, the coarse surface of the support can offer nucleation sites to promote the crystallization of TS-1. The TS-1 nanoparticles formed in the former step can act as the seeds and provide nucleation sites for the later crystallization. Therefore, they can effectively shorten the growth time for later steps.

Furthermore, XRD was applied to prove the successful synthesis of monolithic TS-1/cordierite catalyst (Fig. 3). XRD pattern of TS-1 powders (Fig. 3c) was given for comparison with the TS-1/cordierite catalysts (Fig. 3b) and the cordierite support (Fig. 3a). The XRD pattern of the TS-1/cordierite catalyst showed the characteristic peaks of MFI structure at 2θ=7.9°, 8.9°, 23.1°, 23.9° and 24.4° (indicated by star), which was identical with the standard TS-1 pattern.[11,18] The Ti atom peak at 29.3° (indicated by dot) was a convincing evidence of titanium incorporated in the zeolite framework. Other peaks shown in Fig. 3a were attributed to the cordierite support (indicated by triangle) as compared with Fig 3c. Clearly, none of the distinct peaks in Fig 3b were different from those peaks in the Fig 3a and 3c, which meant the as-prepared catalyst had TS-1 layer grown on the cordierite support.

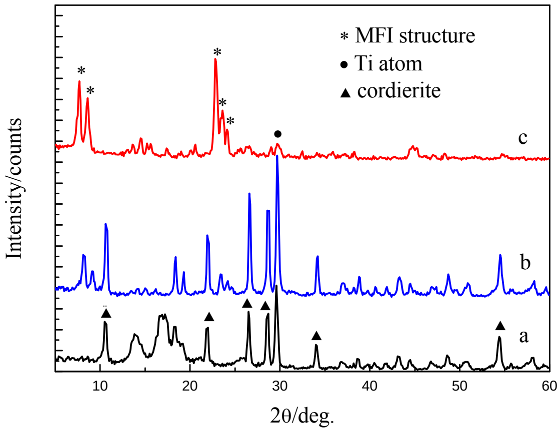


Fig. 3. XRD patterns of (a) the cordierite support, (b) fresh TS-1 layer, and (c) TS-1 powders.

The FT-IR and UV-vis spectra were also employed to further confirm the incorporation of Ti atoms into the framework of the TS-1 crystals. As shown in Fig. 4, the TS-1 layer (b) and powders (c) display the characteristic transmittance bands of MFI zeolite at 1220 cm^{-1}, 1100 cm^{-1}, and 800 cm^{-1}. The band at around 960 cm^{-1} belongs to Ti-O-Si, which had been generally accepted as a direct proof of Ti atoms incorporated into the TS-1 framework.[19,20] The FT-IR results further support that the obtained layer on the monolith is composed of TS-1 powders, and the components in the cordierite do not affect the TS-1 formation in the hydrothermal synthesis. Besides, the corresponding UV-vis spectra of the same samples are shown in Fig. 5. The broad absorbance bands around 210 nm in spectra of the TS-1 catalyst (Fig. 5b, Fig. 5c) belongs to the tetrahedral coordinated, framework titanium.[19] The typical signal of anatase TiO_2 at 330 nm was also detected in the fresh catalysts and as-prepared TS-1 powders.

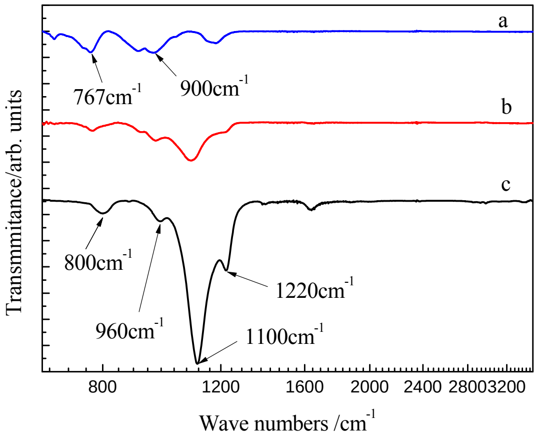


Fig. 4. FT-IR spectra of (a) the cordierite support, (b) fresh TS-1 layer, and (c) TS-1 powders.

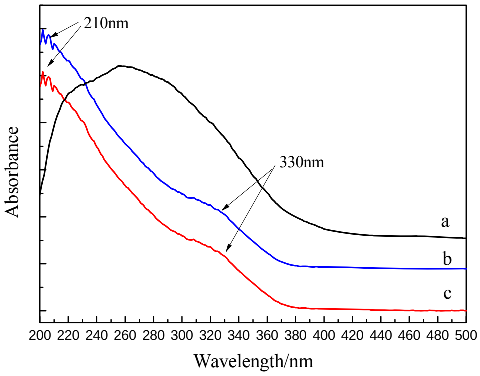


Fig. 5. UV-vis spectra of (a) the cordierite support, (b) fresh TS-1 layer, and (c) TS-1 powders.

3.2. The Characteristics of cyclohexanone ammoximation reaction in monolithic TS-1/cordierite catalysts

In order to compare the characteristics of cyclohexanone ammoximation reaction in monolithic TS-1/cordierite catalysts with and without TBA, a series of experiment were conducted with various influence factors, including reaction temperature, WHSV and channel dimension.

3.2.1 The effect of reaction temperature on cyclohexanone ammoximation reaction

The reaction of cyclohexanone ammoximation was carried out in a continuously operated monolithic reactor as mentioned above. The feed was cyclohexanone, H_2O_2, $NH_3 \cdot H_2O$ at a molar ratio of 1:1.2:1.5. In the range of reaction temperature from 323 to 353 K, the conversions of cyclohexanone increase with the increase of temperature. When the temperature was higher than 353K, the selectivity of oxime decreased from 0.99 to 0.96 respectively (Fig. 6). Similarly, the influence of the temperature was investigated under the existence of co-solvent TBA. The cyclohexanone conversion and oxime selectivity approached 0.96 and 0.99 respectively at the optimal reaction temperature of 343 K.

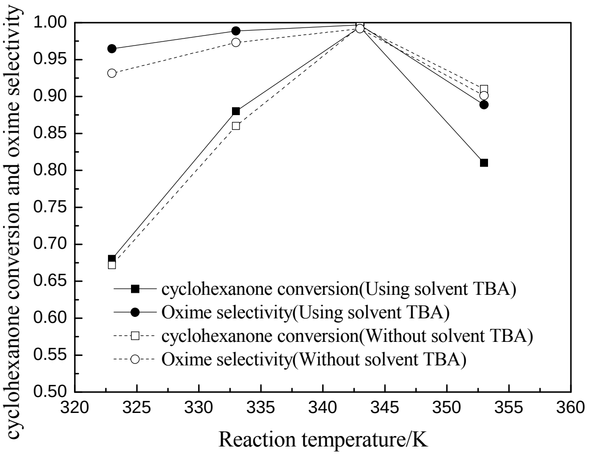


Fig. 6. Effect of reaction temperature on cyclohexanone ammoximation in monolithic TS-1/cordierite catalysts

Feed molar ratio of continuous ammoximation reaction was cyclohexanone: H_2O_2: $NH_3 \cdot H_2O$: TBA=1:1.2:1.5:10(with TBA), cyclohexanone: H_2O_2: $NH_3 \cdot H_2O$ =1:1.2:1.5 (without TBA); WHSV, 6.0 h^{-1}; flow rate of external circulation, 250mL/min; channel density of monolith cordierite, 250cpsi.

3.2.2 Effect of weight hourly space velocity (WHSV)

The WHSV which was calculated by the weight of coated TS-1 layer in equation (4), was also investigated to realize its effect on ammoximation reaction. Within a wide WHSV window from 1.4 to 10 h^{-1}, the cyclohexanone conversion and oxime selectivity without TBA at steady states keep above 0.96 and greater than 0.99, respectively (Fig. 7), which were not obviously different from that in presence of solvent TBA. Therefore, the weight of the loaded catalyst layer is sufficient to achieve a higher conversion of cyclohexanone and selectivity of oxime at WHSV below 10h^{-1}.

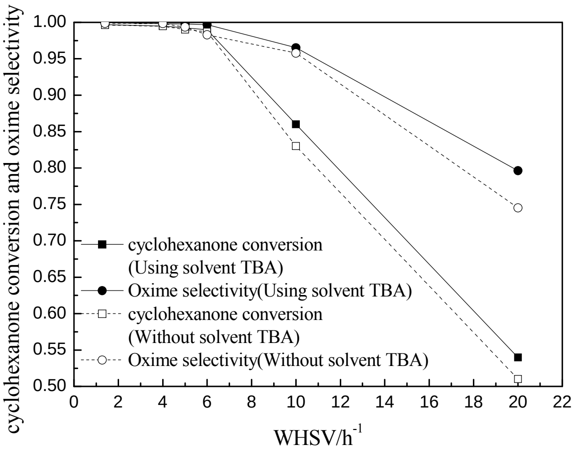


Fig. 7. Effect of WHSV on cyclohexanone ammoximation reaction in monolithic TS-1/cordierite catalysts

Feed molar ratio of continuous ammoximation reaction was cyclohexanone: H_2O_2: $NH_3 \cdot H_2O$: TBA =1:1.2:1.5:10 (with TBA), cyclohexanone: H_2O_2: $NH_3 \cdot H_2O$ =1:1.2:1.5 (without TBA); flow rate of external circulation, 250mL/min; channel density of monolith cordierite, 250cpsi; reaction temperature, 343K.

3.2.3 Influence of channel size of supports to cyclohexanone ammoximation reaction

The monolithic TS-1/cordierite catalysts comprise supports with an array of parallel reaction channels with different size, and the bulk liquids were externally looped through the channels in single phase or two-phase flow corresponding to using or not using solvent TBA. In contrast to the random flow patterns of multiphase in conventional packed beds, the flows in monolithic catalyst bed are highly ordered.[16] The impact of channel size on the ammoximation reaction was tested by using three kinds of monoliths with triangular channels of 2, 1.5, and 1mm in width. As shown in

Fig. 8, at the same WHSV, the 1 mm and 1.5 mm channels give similar conversions and selectivities, which are higher than that in 2 mm channel because of the changes in mass transfer distance and liquid moving speed at the same recycle flow rate.

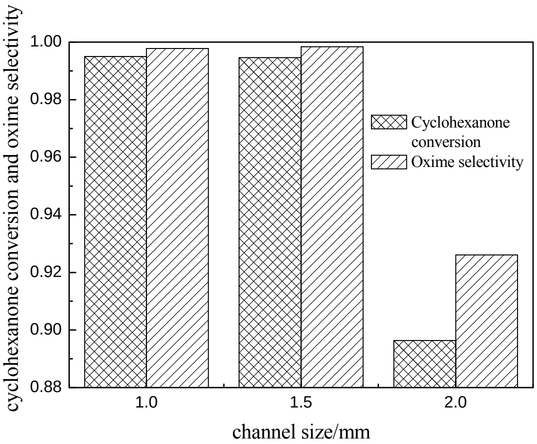


Fig. 8. Effect of channel sizes of monolithic support on cyclohexanone ammoximation reaction

Feed molar ratio of continuous ammoximation reaction was cyclohexanone: H_2O_2: $NH_3{\cdot}H_2O$ =1:1.2:1.5; WHSV, 6.0 h^{-1}; flow rate of external circulation, 250 mL/min; reaction temperature, 343K.

The monolithic reactor with multi-channels of millimeter or sub-millimeter scale is different from conventional fixed bed reactors.[17,21-23] Since the hydraulic diameter of each channel is approached to capillary, liquid-solid surface phenomena may also play a significant role in intensifying mass transfer. The activity results shown in Fig. 8 illustrated that the decrease of channel sizes enhanced the mass transfer and reaction. When the reaction operated at the same external looping rate, liquid surface tension dominated in heterogeneous ammoximation reaction compared with inertia force, and the formation of Taylor’s flow will benefit to intensify mass transfer in the millimeter-scaled channels.[24,25]

3.3. Activity and lifetime of monolithic TS-1/cordierite catalysts

The catalyst deactivation is a critical problem for the ammoximation reaction of cyclohexanone. Therefore, it is necessary to investigate the feasibility and activity stability of the monolithic TS-1/cordierite catalyst. The reaction was run for over 50 h of time on stream (TOS), and the experimental data were presented in Fig. 9. In Fig. 9a-d the conversions were nearly 0.98 at the primary steady stage and then remained until the deactivation, while the selectivities increase at the primary stage, then remained at 0.99 for a long period, and finally decreased to 0.90. Comparing with slurry bed reactor [4,26] and membrane reactor,[27,28] the monolithic reactor displayed much longer operating stability and feasibility in the continuous ammoximation reaction. Fig. 9b recorded the reaction data without TBA, which were similar to that with TBA shown in Fig. 9c. Due to the merits of monolithic support, multi-channels in monolithic TS-1/cordierite catalysts provided well mixing between cyclohexanone in organic phase and H_2O_2, $NH_3{\cdot}H_2O$ in water phase without TBA, and finally intensified the multiphase reaction.

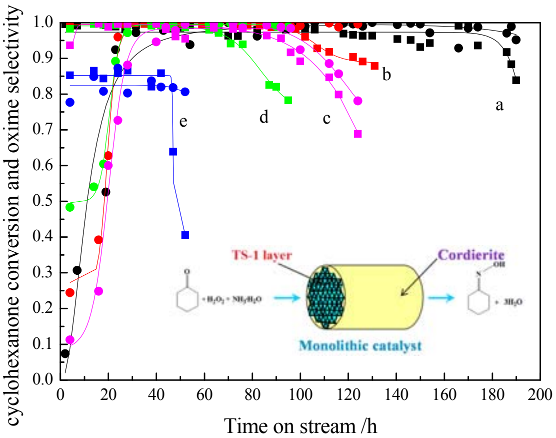


Fig. 9. Performances of different WHSVs for continuous cyclohexanone ammoximation in monolithic TS-1/cordierite catalysts

The cyclohexanone conversion, X and the oxime selectivity, S: (a) X ■, S ● ,WHSV=1.4 h^{-1}, without TBA; (b) X ■, S ● , WHSV=6 h^{-1}, without TBA; (c) X ■, S ●, WHSV=6 h^{-1}, with TBA; (d) X ■, S ●, WHSV=10 h^{-1}, without TBA; (e) X ■, S ●, WHSV=20 h^{-1}, without TBA in the ammoximation;

Feed molar ratio of continuous ammoximation reaction was cyclohexanone: H_2O_2: $NH_3{\cdot}H_2O$: TBA =1:1.2:1.5:10 (with TBA), cyclohexanone: H_2O_2: $NH_3{\cdot}H_2O$ =1:1.2:1.5 (without TBA); flow rate of external circulation, 250mL/min; channel density of monolith cordierite, 250cpsi; reaction temperature, 343K.

In Fig. 9e at a high WHSV of 20 h^{-1}, the cyclohexanone conversion and oxime selectivity at steady state maintained at about 0.80, because the reaction is not enough. The activity of monolithic TS-1/cordierite catalyst declined sharply within a short time whether solvent TBA was adopted or not in continuous ammoximation reaction (Fig.10). The activity was defined as equation (3), which was high under WHSV below 10 h^{-1}, and low under WHSV up to 20 h^{-1}. Except for the high catalytic activity, the applicability of monolithic TS-1/cordierite catalysts also depended also on their lifetime and stability. The deactivation was considered to start when the activity decreased to 0.92. Fig. 10b and 10c illustrated that the lifetimes of the monolithic TS-1/cordierite catalysts without solvent TBA exhibited a bit longer than that with solvent. In addition, the solvent TBA was beneficial to mass transfer but would accelerated deactivation of TS-1 catalyst.[4]

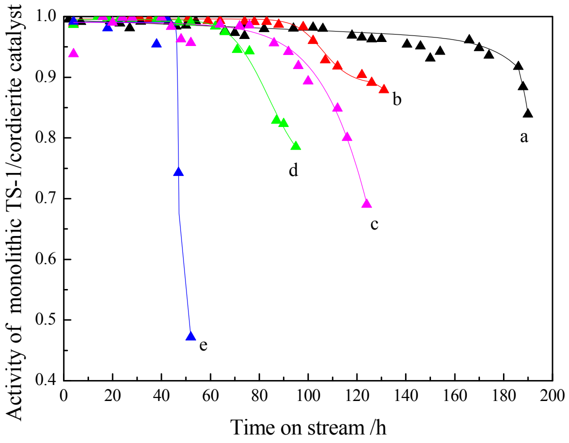


Fig. 10. Variation of activity under different WHSVs for continuous cyclohexanone

ammoximation in monolithic TS-1/cordierite catalysts

The activity, a: (a) ▲, WHSV=1.4 h^{-1}, without TBA; (b) ▲, WHSV=6 h^{-1}, without TBA; (c) ▲, WHSV=6 h^{-1}, with TBA; (d) ▲, WHSV=10h^{-1}, without TBA; (e) ▲, WHSV=20 h^{-1}, without TBA of the ammoximation;

Feed molar ratio of continuous ammoximation reaction was cyclohexanone: H_2O_2: $NH_3\cdot H_2O$: TBA =1:1.2:1.5:10 (with TBA), cyclohexanone: H_2O_2: $NH_3\cdot H_2O$ =1:1.2:1.5 (without TBA); flow rate of external circulation, 250mL/min; channel density of monolith cordierite, 250cpsi; reaction temperature, 343K.

From the curves in Fig. 10, the deactivation rates of monolithic TS-1/cordierite catalyst obey the trend of $-\frac{da}{dt}\Big|_{\substack{WHSV=1.4h^{-1}\\ a=0.92}} < -\frac{da}{dt}\Big|_{\substack{WHSV=6h^{-1}\\ a=0.92}} < -\frac{da}{dt}\Big|_{\substack{WHSV=10h^{-1}\\ a=0.92}} < -\frac{da}{dt}\Big|_{\substack{WHSV=20h^{-1}\\ a=0.92}}$. The lifetime of monolithic TS-1/cordierite catalyst strongly depends on WHSV, because WHSV directly affects the formation of precursor of coke and causes deactivation of TS-1 catalysts (Fig. 11).The result shown in Fig. 11 is obtained at the optimal reaction temperature for different WHSVs and keeping other conditions the same as that in Fig. 10. Rapid deactivation of the monolithic TS-1/cordierite catalyst occurred under high WHSV, and was related directly to the residual amounts of unreacted H_2O_2 and $NH_3\cdot H_2O$, causing side reactions, such as forming precursor of coking and leaching titanium from TS-1 framework.

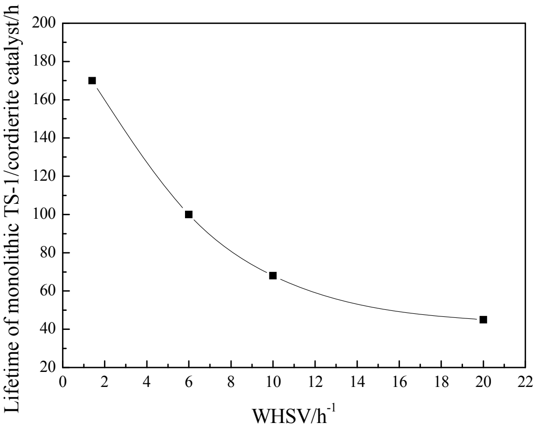


Fig. 11. Variation of lifetime under different WHSVs for continuous cyclohexanone ammoximation without TBA in monolithic TS-1/cordierite catalysts

Feed molar ratio of continuous ammoximation reaction was cyclohexanone: H_2O_2: $NH_3 \cdot H_2O$ =1:1.2:1.5; flow rate of external circulation, 250mL/min; Channel density of monolith cordierite, 250cpsi; Reaction temperature, 343K.

To illustrate the deactivation reasons, the deactivated catalyst used for TOSs of 130 hours was characterized by the XRD, UV-vis and FT-IR, respectively. The XRD patterns verified that the used catalyst still possessed the typical MFI structure, but the crystallinity decreased (Fig.S2), even though they were calcined in air at 823K. Besides, UV-vis spectra of the deactivated catalysts described that the intensity of the absorbance band round 330 nm had increased (Fig.S3). It was demonstrated that the anatase TiO_2 was easier to form attributed to the collapse of skeleton in alkaline reaction conditions.[29] The deactivation attributed to the change of the catalyst structure would be irreversible.

EDS analyses conducted on the surface of monolithic TS-1 layer samples revealed the presence of Si, Ti and O atoms (Fig.S4). According to the EDS data (see Table 1), Si/Ti molar ratio of the deactivated TS-1 layer obtained from continuous ammoximation with

TBA get larger than that without TBA. The Si/Ti molar ratio of the deactivated TS-1 layer obtained from continuous ammoximation without TBA was about 28.57, and had little change compared with the fresh TS-1 layer. It also proved that the skeleton collapsing degree was affected by the alkalinity of ammoximation reaction solution. The introduction of the solvent TBA would increase the alkalinity of ammoximation reaction solution.

Table 1 EDS analysis of various TS-1 layer samples

Samples	Actual Element (atom%)			Si/Ti
	O	Si	Ti	
1	80.96±1.46	18.36±0.42	0.68±0.12	27.00
2	75.89±1.37	23.42±0.32	0.70±0.09	33.46
3	74.27±1.43	24.86±0.25	0.87±0.09	28.57

Samples: 1, Fresh TS-1 layer; 2, Deactivated TS-1 layer obtained from continuous ammoximation with TBA (TOS 124 h); 3, Deactivated TS-1 layer obtained from continuous ammoximation without TBA (TOS 130 h).

The FT-IR spectra of the fresh TS-1 layer in Fig. 4b and deactivated TS-1 layer in Fig. 12 displayed all the characteristic bands of MFI zeolite, Although the intensities of band around the 960 and 800 cm^{-1} bands decline after deactivation, the ratio of I_{960}/I_{800} remains unchanged, which was different from that in continuous ammoximation reaction with solvent TBA.[4,30] The bands in the range of 2900-3000 cm^{-1}, assign to the stretching of saturated C-H bonds, which disappear completely when the deactivated catalyst was calcined in air at 823K as shown in Fig. 12b. The high-molecular-weight byproducts will block the pore mouths of TS-1 catalyst, and cause fast deactivation.

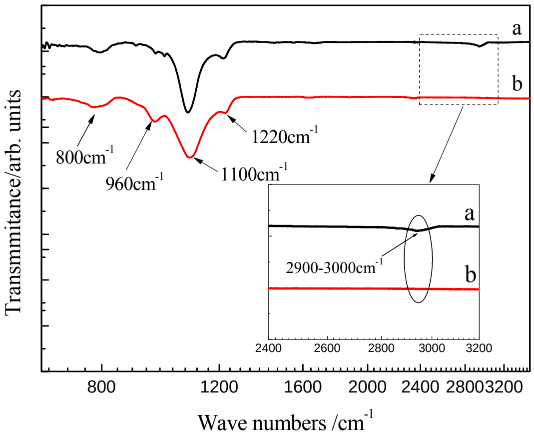


Fig. 12. FT-IR spectra of (a) deactivated TS-1 layer obtained from continuous ammoximation without TBA and (b) the same deactivated TS-1 layer calcined in air at 823K for 6 h

4. Conclusions

The monolithic TS-1/cordierite catalysts prepared by hydrothermal synthesis exhibited well catalytic activity in continuous cyclohexanone ammoximation reaction. Heterogeneous cyclohexanone ammoximation reaction without organic solvent TBA was intensified in the monolithic TS-1/cordierite catalyst, attributed to that the multi-channels of millimeter or sub-millimeter scale effectively decreased external mass transfer. Thereupon the cyclohexanone conversion and oxime selectivity within a wide WHSV range from 1.4 to 10h^{-1} were able to retain almost above 0.96 and 0.98 respectively at the optimal reaction temperature of 343 K. The processes can enormously reduce subsequent separating cost. Moreover, the lifetime of monolithic TS-1/cordierite catalysts in heterogeneous continuous ammoximation reaction solvent free exhibited a longer than that with TBA.

Acknowledgments

We acknowledge the financial support from the National Natural Science Foundation of China (Project No. 20876109 and 21276180) and the program for Changjiang Scholars and Innovative

Research Team in University (IRT0936).

Notes

[a] *School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*

[b] *Tianjin Key Laboratory of Marin Resources and Chemistry, Tianjin University of Science and Technology, Tianjin 300457, China*

[*] *Corresponding author: E-mail: xinf@tju.edu.cn (F. Xin), Tel. 86-22-27409533, Fax. 86-22-27892359.*

References

1. G. Bellussi and M. S. Rigutto, in *Studies in Surface Science and Catalysis*, eds. E. M. F. P. A. J. H. van Bekkum and J. C. Jansen, Elsevier, 2001, vol. 137, pp. 911-955.
2. H. Ichihashi and H. Sato, *Applied Catalysis A: General*, 2001, **221**, 359-366.
3. A. Cesana, M. A. Mantegazza and M. Pastori, *Journal of Molecular Catalysis A: Chemical*, 1997, **117**, 367-373.
4. X. Zhang, Y. Wang and F. Xin, *Applied Catalysis A: General*, 2006, **307**, 222-230.
5. J. E. Gallot, D. Trong On, M. P. Kapoor and S. Kaliaguine, *Industrial & Engineering Chemistry Research*, 1997, **36**, 3458-3467.
6. F. Bonino, A. Damin, S. Bordiga, C. Lamberti and A. Zecchina, *Langmuir*, 2003, **19**, 2155-2161.
7. F. Bonino, A. Damin, G. Ricchiardi, M. Ricci, G. Spanò, R. D'Aloisio, A. Zecchina, C. Lamberti, C. Prestipino and S. Bordiga, *The Journal of Physical Chemistry B*, 2004, **108**, 3573-3583.
8. A. Renken, in *Basic Principles in Applied Catalysis*, ed. M. Baerns, Springer Berlin Heidelberg, 2004, vol. 75, pp. 521-542.
9. W. O. Parker and R. Millini, *Journal of the American Chemical Society*, 2006, **128**, 1450-1451.

10. Z. Zhong, X. Liu, R. Chen, W. Xing and N. Xu, *Industrial & Engineering Chemistry Research*, 2009, **48**, 4933-4938.
11. M. Taramasso and G. Perego, Snam Progetti, 1983, *US*4410501A.
12. Y. G. Li, Y. M. Lee and J. F. Porter, *Journal of Materials Science*, 2002, **37**, 1959-1965.
13. Z. Lai, G. Bonilla, I. Diaz, J. G. Nery, K. Sujaoti, M. A. Amat, E. Kokkoli, O. Terasaki, R. W. Thompson, M. Tsapatsis and D. G. Vlachos, *Science*, 2003, **300**, 456-460.
14. Z. Zhuang, X. Jiang, D. Y. Peng, W. J. Lv and F. Xin, *Materials Research Innovations*, 2013, **17**, 490-494.
15. L. Dal Pozzo, G. Fornasari and T. Monti, *Catalysis Communications*, 2002, **3**, 369-375.
16. R. K. Edvinsson and A. Cybulski, *Catalysis Today*, 1995, **24**, 173-179.
17. M. T. Kreutzer, P. Du, J. J. Heiszwolf, F. Kapteijn and J. A. Moulijn, *Chemical Engineering Science*, 2001, **56**, 6015-6023.
18. X. Wang, X. Zhang, H. Liu, K. L. Yeung and J. Wang, *Chemical Engineering Journal*, 2010, **156**, 562-570.
19. M. R. Boccuti, K. M. Rao, A. Zecchina, G. Leofanti and G. Petrini, in *Studies in Surface Science and Catalysis*, eds. A. Z. Claudio Morterra and C. Giacomo, Elsevier, 1989, vol. Volume 48, pp. 133-144.
20. G. Ricchiardi, A. Damin, S. Bordiga, C. Lamberti, G. Spanò, F. Rivetti and A. Zecchina, *Journal of the American Chemical Society*, 2001, **123**, 11409-11419.
21. Z. R. Ismagilov, R. A. Shkrabina, S. A. Yashnik, N. V. Shikina, I. P. Andrievskaya, S. R. Khairulin, V. A. Ushakov, J. A. Moulijn and I. V. Babich, *Catalysis Today*, 2001, **69**, 351-356.
22. M. T. Kreutzer, P. Du, J. J. Heiszwolf, F. Kapteijn and J. A. Moulijn, *Chemical Engineering*

Science, 2001, **56**, 6015-6023.

23. A. Stankiewicz, *Chemical Engineering Science*, 2001, **56**, 359-364.

24. R. K. Edvinsson and S. Irandoust, *AIChE Journal*, 1996, **42**, 1815-1823.

25. N. Shao, A. Gavriilidis and P. Angeli, *Chemical Engineering Journal*, 2010, **160**, 873-881.

26. N. Liu, H. Guo, X. Wang, L. Chen and Y. Chen, *Chinese Journal of Catalysis*, 2003, **24**, 441-446.

27. Z. Li, R. Chen, W. Xing, W. Jin and N. Xu, *Industrial & Engineering Chemistry Research*, 2010, **49**, 6309-6316.

28. Z. Zhong, W. Xing, X. Liu, W. Jin and N. Xu, *Journal of Membrane Science*, 2007, **301**, 67-75.

29. A. Zheng, C. Xia, Y. Xiang, M. Xin, B. Zhu, M. Lin, G. Xu and X. Shu, *Catalysis Communications*, 2014, **45**, 34-38.

30. C. Wu, Y. Wang, Z. Mi, L. Xue, W. Wu, E. Min, S. Han, F. He and S. Fu, *Reaction Kinetics and Catalysis Letters*, 2002, **77**, 73-81.