Chemical Engineering Journal 156 (2010) 418–422

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Scouring-ball effect of microsized silica particles on operation stability of the membrane reactor for acetone ammoximation over TS-1

Rizhi Chen, Zhen Bu, Zhaohui Li, Zhaoxiang Zhong, Wanqin Jin, Weihong Xing*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering,
Nanjing University of Technology, No. 5 Xinmofan Road, Nanjing 210009, PR China

ARTICLE INFO

Article history:
Received 11 September 2009
Received in revised form 28 October 2009
Accepted 2 November 2009

Keywords:
Titanium silicalite-1
Acetone ammoximation
Acetone oxime
Ceramic membrane reactor

ABSTRACT

A ceramic membrane reactor system was developed for the continuous ammoximation of acetone to acetone oxime over titanium silicalites-1 (TS-1) catalysts. The effects of catalyst concentration and microsized silica particles on the performances of the membrane reactor system were examined in detail. For the membrane reactor system the optimal catalyst concentration is 17.0 g L^{-1}, obviously higher than the one obtained from the previous experiments in a batch glass reactor, because the strong adhesion of TS-1 catalyst particles on the surface of the pipeline, the tank and the membrane leads to the decrease of effective catalyst concentration. Adding the microsized silica particles can effectively inhibit the decrease of TS-1 catalysts concentration in reaction slurry and improve the operation stability of the membrane reactor system significantly, benefiting from the scouring effect and the attachment of TS-1 particles on the surfaces of larger silica particles. According to the estimation of hydrodynamic forces acting on particles, microsized silica particles are hard to deposit on the contact surfaces at the studied conditions and therefore a longer stable operation of the membrane reactor system has been achieved.

1. Introduction

Heterogeneous catalysts are widely used in chemical production processes. These catalysts can work under the form of powder suspended in a slurry or can be immobilized on various supports, such as glass, quartz, stainless steel or membrane [1,2]. In the case of a catalyst fixed on a carrier material, the drawbacks are mass transfer limitations of reactants to the surface of the catalyst and the decrease of effective surface area of the catalyst particles. It was reported that catalysts in suspension have a better efficiency than immobilized ones [3–5]. In this process, however, the separation of catalysts from the products creates another problem to be solved in practical applications, especially for the ultrafine particles, since it is directly associated with the product purity and the operational cost [6].

One of the promising methods to solve the above mentioned problem is to couple the heterogeneous catalytic reaction with membrane separation to structure a membrane reactor, in which the membrane facilitates the in situ separation of fine catalysts from the reaction mixture. The concept of membrane reactor is based on the potential of semipermeable membranes to retain the catalyst but not the reactants or products formed during the reaction [7–9]. A membrane reactor allows operation in continuous systems without the need to separate the catalyst from the reaction ambient. In addition, the system is easy to operate, control and scale-up. At present, most works were mainly focused on the biochemical processes and wastewater treatment, and basically used polymeric membranes [10–12]. Up to date, there are few researches based on the chemical or petrochemical processes. Because of its advantages such as good chemical stability and favorable mechanical strength, ceramic membranes can be used in severe reaction conditions [13–15]. Therefore, in this work, a ceramic membrane reactor system was developed.

To investigate the continuous process of ceramic membrane reactor experimentally, the acetone ammoximation to acetone oxime over TS-1 was taken as a model reaction for the following reasons. Acetone oxime is a kind of deoxidant with high deoxidization effect, low toxicity and low environmental pollution, which is widely used as corrosion inhibitor and passivator in boiler passivation solution of fire power plant instead of N_2H_4 [16]. Acetone ammoximation catalyzed by TS-1 employing NH_3 and H_2O_2 as the ammoximation agents is a promising process for preparing acetone oxime due to its high catalysis efficiency and low environment pollution compared to the traditional production processes [17].

With respect to the membrane reactor system, an important consideration is the long-term operation stability, which is a key factor affecting the economic and commercial viability of the system. In this system, adhesion of TS-1 catalysts and Si dissolution are suggested as causes for the unstable operation. On one hand,

---

* Corresponding author. Tel.: +86 025 83172288; fax: +86 025 83172292.
E-mail address: xingwh@njut.edu.cn (W. Xing).

1385-8947/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.cej.2009.11.001

due to the small particle size, TS-1 catalysts adhere easily on the surfaces of the pipeline, the tank and the membrane, which will cause the decrease of catalyst concentration in reaction slurry and lead to consequent decline in reaction rate and permeate flux of the membrane. On the other hand, the basic reaction medium in the presence of ammonia can lead to Si dissolution away from the titanium silicalite framework and the consequent deactivation of the TS-1 catalyst [18]. In order to keep the system stable, it is needed to supply the fresh TS-1 catalysts and clean the membrane. In our previous works [13,19], microsized particles such as silica and alumina have been used to inhibit the adhesion of ultrafine catalyst particles on the contact surfaces, because of their scouring effect. A liquid Si-containing assistant [20] and solid silica particles [18] have been tried to inhibit the Si dissolution in the ammoximation of cyclohexanone to the cyclohexanone oxime over TS-1. However, there is no report addressing the inhibition effect of adding particles on both adhesion and dissolution of catalysts in a membrane reactor system.

In the present research, microsized silica particles were added into the membrane reactor system and the effects of silica particles on the performances of TS-1 and filtration resistance were investigated preliminarily to develop a method that can improve the operation stability of the membrane reactor system for the acetone ammoximation to acetone oxime over TS-1. The effect of TS-1 catalyst concentration on the performances of the ceramic membrane reactor system was also studied and compared to the result obtained from the previous experiments in a batch glass reactor.

2. Experimental

2.1. Materials

TS-1 catalyst (average particle size, 200 nm; specific surface area, 95 $m^2 g^{-1}$; the Si/Ti mass ratio, 9) was provided by Baling Petrochemical Company, SINOPEC [6]. Silica with an average particle size of 35 μm was provided by Shanton Xilong Chemical Factory, China. Acetone was provided by Shanghai Kaidi Experiment Reagent, China; 30% hydrogen peroxide by Sinopharm Chemical Reagent, China; 25% ammonia solution by Chengdu Kelong Chemical Reagent, China; *t*-butanol by Nanjing Fubang Chemical Co. Ltd., China; methanol (>99.9% Chromatography Grade) by Yuwang Group, China and pure water by Hangzhou Wahaha Group, China. Deionized water (electrical conductivity <12 μs cm^{-1}) was self-made with RO membrane.

2.2. Ceramic membrane reactor system

The ceramic membrane reactor system, as shown in Fig. 1, was designed and constructed on a laboratory scale, which consisted mainly of a slurry tank, a centrifugal pump, a cross-flow ceramic membrane module, feed system, and products collecting system and heating system. The slurry tank was made of stainless steel with a working volume of 2 L, which was equipped with an external jacket for temperature controlling. Tubular ceramic membrane, provided by Nanjing Jiusi High-Tech Co. Ltd., China, with 12 mm outer diameter, 8 mm inner diameter and a filtration area of 43 cm^2 was used in this work. The membrane has an asymmetrical structure in which a thin layer of ZrO_2 with nominal pore size of 0.2 μm was coated on the inner wall of a tubular α-Al_2O_3 porous support. Three controlled volume pumps (Baoding Lange constant-flow pump Co. Ltd., China) were used to feed ammonia solution, acetone solution and hydrogen peroxide solution to the system separately. A centrifugal pump (Grundfos, Denmark) was used to pump the feed suspension through the membrane module.

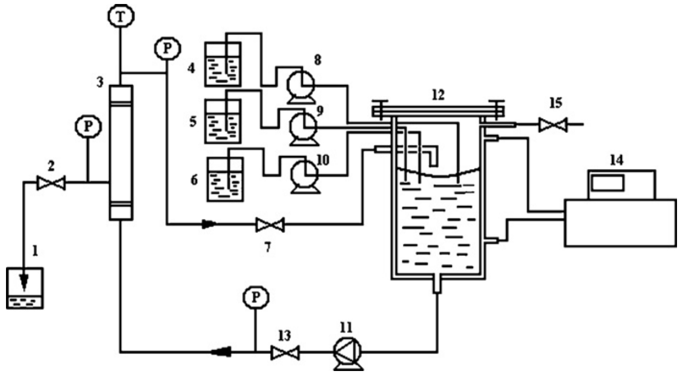


Fig. 1. Diagram of ceramic membrane reactor system for acetone ammoximation to acetone oxime: (1) reaction mixture receiver; (2, 7, 13, and 15) valves; (3) membrane module; (4) reserve tank of acetone solution; (5) reserve tank of ammonia solution; (6) reserve tank of hydrogen peroxide solution; (8) acetone solution feed pump; (9) ammonia solution feed pump; (10) hydrogen peroxide solution feed pump; (11) centrifugal pump; (12) reactor; (14) thermostatic batch.

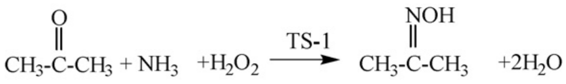
2.3. Ammoximation experiments

The acetone ammoximation to acetone oxime over TS-1 (Scheme 1) was carried out in the ceramic membrane reactor system.

After 3.5 mol acetone in 1.7 L *t*-butanol solution and TS-1 catalysts (with or without silica particles) were added into the reactor, the reactor was sealed and the centrifugal pump was turn on, and then the reactor system was heated by circulating hot water through the jacket of reactor used. When the temperature reached the set value, the ammonia solution, acetone solution and hydrogen peroxide solution were feed continuously into the membrane reactor, and the ammoximation reaction started. After reacting for 1 h, the feeding was stopped and the reaction was run for 2 h again. Then the feeding was opened once more and meanwhile the products flowed out from the system at a certain flow rate by controlling the valve 2 shown in Fig. 1, equaling to the total feed flow rate. Thus, the liquid level in the reactor was kept constant and the system was operated in a constant membrane flux. The products were collected in a 500 mL graduated cylinder. The catalysts particles were completely retained in the reactor by the ceramic membrane. Each continuous ammoximation run was conducted for 6 h with respect to the investigations of operation conditions. Operation parameters were as follows (except special explanations): acetone concentration in the feed 1.8 mol L^{-1}, H_2O_2/acetone = 1.2 (mol), NH_3/acetone = 2.2 (mol), reaction temperature 70 °C, total feed flow rate 12 mL min^{-1}.

After each run, the system was emptied and thoroughly rinsed with top water to remove residual reaction mixture; the membrane was cleaned by circulating 1 wt% NaOH solution at 60 °C and 1 wt% HNO_3 solution at 30 °C for several hours with the permeate line open, followed by thorough rinsing with deionized water. Then the deionized water permeability through the membrane was measured to assess the cleanliness of the membrane. As the water permeation flux of the used membrane was greater than 95% that of the fresh membrane, the membrane was regarded as clean and used for the next run.

In some cases, after reaction the concentration of TS-1 catalysts in suspension was evaluated by the gravimetric method,



$$CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 + NH_3 + H_2O_2 \xrightarrow{\text{TS-1}} CH_3\text{-}\overset{\overset{\displaystyle NOH}{\|}}{C}\text{-}CH_3 + 2H_2O$$

Scheme 1. Acetone ammoximation to acetone oxime over TS-1.

and the concentration of silicium and titanium element in the permeate were analyzed by inductively coupled plasma emission spectroscopy (ICP, Optima 2000DV).

The products were taken from the outlet of the reactor regularly after the reactor operated continuously and analyzed by a HPLC system (Agilent 1100 Series, USA) equipped with a diode array detector (DAD) and an auto-sampler. Chromatographic separations were performed at 35 °C using a ZORBAX Eclipse XDB-C18, 5 μm, 4.6 mm × 250 mm column. A mobile phase composed of 25% methanol and 75% water at a flow rate of $1\,\mathrm{mL\,min^{-1}}$ was used. Acetone conversion and acetone oxime selectivity were calculated based on the starting amount of acetone, according to the Eqs. (1) and (2), respectively:

$$X = \frac{C_{\mathrm{acetone(o)}} - C_{\mathrm{acetone(P)}}}{C_{\mathrm{acetone(o)}}} \times 100\% \tag{1}$$

$$S = \frac{C_{\mathrm{AO}}}{C_{\mathrm{acetone(o)}} - C_{\mathrm{acetone(P)}}} \times 100\% \tag{2}$$

where X is the acetone conversion, S the acetone oxime selectivity, $C_{\mathrm{acetone(o)}}$ the initial acetone concentration in the feed ($\mathrm{mol\,L^{-1}}$), $C_{\mathrm{acetone(P)}}$ the acetone concentration in the outlet of the reactor ($\mathrm{mol\,L^{-1}}$), and C_{AO} the concentration of acetone oxime in the outlet of the reactor ($\mathrm{mol\,L^{-1}}$).

The filtration resistance was obtained from the transmembrane pressure and the membrane flux according to the Darcy law [21]:

$$R = \frac{\Delta P}{J\mu} \tag{3}$$

where R is the filtration resistance ($\mathrm{m^{-1}}$), ΔP the transmembrane pressure (Pa), J the membrane flux ($\mathrm{m\,s^{-1}}$) and μ the viscosity of permeate (Pa s).

3. Results and discussion

3.1. Effect of catalyst concentration

In our previous work, the reaction conditions of acetone ammoximation over TS-1 had been optimized in a batch glass reactor by single factor experiments, including the molar ratio of NH_3/acetone, the molar ratio of H_2O_2/acetone, the acetone concentration, the reaction temperature, the reaction time, the catalyst concentration, and so on [22]. However, when the acetone ammoximation over TS-1 was carried out in the membrane reactor system, the ultrafine TS-1catalyst particles might adhere on the contact surfaces, resulting in a decrease of effective catalyst concentration. Therefore, the effect of catalyst concentration on the system was first examined aiming to find an optimal catalyst concentration.

Fig. 2 shows the effect of the TS-1 catalyst concentration on the performances of the ceramic membrane reactor system without silica particles. It is found that with increasing the catalyst concentration the conversion and selectivity first increases until a catalyst concentration of $17.0\,\mathrm{g\,L^{-1}}$ and then keeps constant. Similar result was found by Saxena et al. [23] in the ammoximation of cyclohexanone to cyclohexanone oxime over nanoporous TS-1. It is well known that the catalyst concentration has a great effect on the reaction rate in a certain concentration range [24]. So the acetone conversion increases with increasing the catalyst concentration until the catalyst concentration is enough for the reaction. The liquid phase acetone ammoximation over TS-1 follows the hydroxylamine route: the ammonia is first oxidized to the hydroxylamine intermediate by the hydrogen peroxide over TS-1 and then the hydroxylamine reacts with the acetone in the homogeneous phase to form the acetone oxime [17]. Therefore, as the TS-1 catalyst concentration is lower, the ammonia and hydrogen peroxide added into the reactor cannot be transformed to the hydroxylamine in time, and then the acetone will have more chances to react with the excess ammonia and hydrogen peroxide to form by-products, resulting in a lower selectivity [25]. It is noted from Fig. 2 that the filtration resistance keeps constant in the studied experimental range possibly due to the lower membrane flux of $167.4\,\mathrm{L\,m^{-2}\,h^{-1}}$ (the corresponding discharge rate is $12\,\mathrm{mL\,min^{-1}}$). According to the discussion, for the membrane reactor system the suitable catalyst concentration is $17.0\,\mathrm{g\,L^{-1}}$, obviously higher than the optimized catalyst concentration of $4.9\,\mathrm{g\,L^{-1}}$ obtained in a batch glass reactor by single factor experiments [22], which could be due to the adhesion of TS-1 catalyst particles on the contact surfaces in the system. Moreover, as the catalyst concentration was $4.9\,\mathrm{g\,L^{-1}}$ in the membrane reactor system, the pressure in the reactor was higher because the added ammonia and hydrogen peroxide was not transformed in time, which made the feeding stop and the reaction process failure.

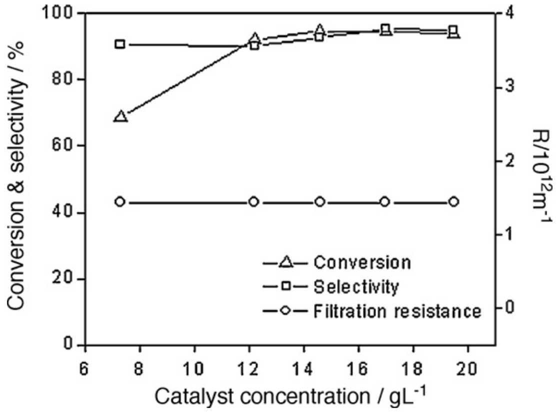


Fig. 2. Effect of catalyst concentration on the conversion, selectivity of acetone ammoximation and the filtration resistance.

3.2. Continuous run of the ceramic membrane reactor system

The continuous acetone ammoximation to acetone oxime over TS-1 in the membrane reactor system was performed at a TS-1 catalyst concentration of $17.0\,\mathrm{g\,L^{-1}}$ without or with silica particles ($12.0\,\mathrm{g\,L^{-1}}$), respectively, and the results are shown in Fig. 3.

With respect to the system without silica particles, the conversion is almost about 93% within the first 10 h and then decreases gradually to 76% at the operation time of 21 h, while the selectivity first increases at the primary stage, then keeps at about 95% until 17 h, and finally decreases to 89%. The strong adhesion of TS-1 catalyst particles on the surfaces of the pipeline, the tank and the membrane should be responsible for the decline of the performances of the membrane reactor, which is confirmed by the analysis of the TS-1 catalyst concentration in suspension. As presented in Table 1, after 21 h of operation, the TS-1 catalyst concentration in suspension decreases to $3\,\mathrm{g\,L^{-1}}$, only about 17.6% that of the initial one. The dissolved Si in the permeate keeps at about $2\,\mathrm{mg\,L^{-1}}$, and the dissolved Ti is closed to zero in agreement with the reports [18,20]. According to the ICP analysis, the decreased TS-1 catalyst concentration due to the dissolution is estimated to be

Table 1
Change of the concentration of TS-1 catalyst in suspension in the membrane reactor system.

System	Catalyst concentration/g L^{-1}	
	Initial	After reaction
Without silica	17	3
With silica	17	6

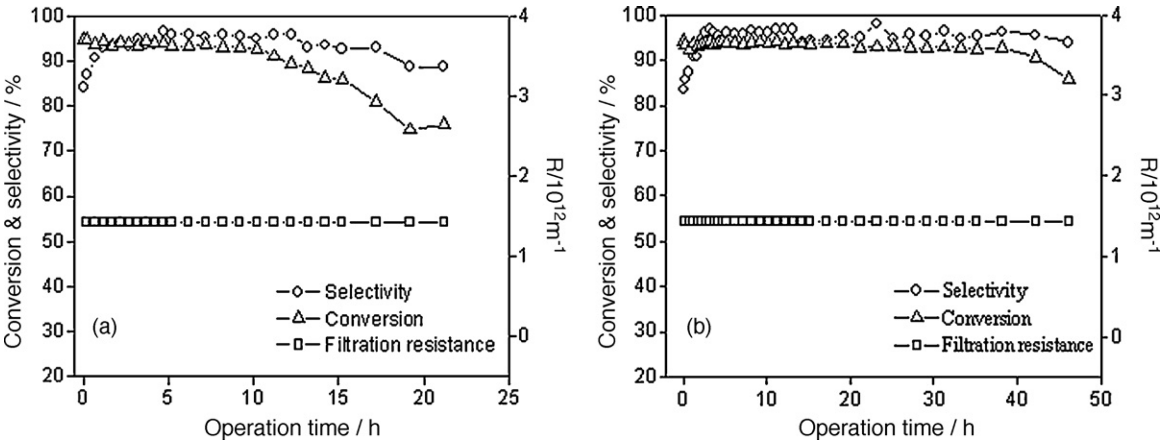


Fig. 3. Long-term operation stability of the continuous ceramic membrane system: (a) without silica particles and (b) with silica particles.

only about 28 mg L^{-1} after 21 h of continuous run because the dissolution process of Si in the reaction slurry is very slow, which can be ignored in the short-term run of the membrane reactor system [18,20]. So, the decrease of TS-1 catalyst concentration is mainly caused by the adhesion. As presented in Fig. 2, the TS-1 catalyst concentration can obviously affect the conversion and selectivity of the acetone ammoximation. Therefore, the strong adhesion of TS-1 catalysts should be one of the main reasons for the decline of the membrane reactor performances. It is seen from Fig. 3(a) that the filtration resistance keeps stable throughout the entire experiment period, possibly because the adhesion of catalyst particles on the membrane surface saturates quickly during the batch operation, and leads to a constant thickness of filter cake and therefore, a stable filtration resistance.

It is interesting to find from Fig. 3(b) that as the microsized silica particles were added into the system, the performances of the membrane reactor are improved obviously. For example, the conversion keeps at about 93% until 37 h, and the conversion at the operation time of 46 h is about 86% higher than the one at the operation time of 21 h without silica particles. The phenomena can be explained by the fact: the addition of silica particles effectively decreases the adhesion of TS-1 catalyst particles on the contact surfaces. As shown in Table 1, after 46 h of operation, the TS-1 catalyst concentration in suspension is 6 g L^{-1}, obviously higher than the one without silica. The dissolved Si in the permeate keeps at about 2.5 mg L^{-1} larger than the one without silica particles, because the added silica particles can also be dissolved in the basic reaction medium. Similar with the system without silica particles, the dissolved TS-1 catalysts can also be ignored. Therefore, the improvement of membrane reactor performances is mainly owed to the decrease of TS-1 catalysts adhesion. Additionally, the addition of silica particles does not result in the change of the filtration resistance. The result is somewhat different from that reported in our previous studies [18,19], which might be due to the lower membrane flux as mentioned above.

The results indicate that silica particles have a significant influence on the operation stability of the ceramic membrane reactor system. They might have a "scouring-ball" effect that removes the already deposited TS-1 away from the contact surfaces [18] to maintain the effective catalyst concentration. This can be explained by the deposition behavior of TS-1 particles and silica particles on the contact surfaces. To understand their deposition behavior, the forces acting on a single particle should be considered. There are two normal forces acting upon a particle on the contact surfaces, which are the adhesion force of neighboring particles F_a and the lift force F_l. A detailed description of these forces was given in other references [18,26]. The adhesion force of interacting particles is typically van der Waals force F_{vdW} [18], which can be calculated according to the following equation:

$$F_a = F_{vdW} = \frac{\hbar\varpi d_P}{32\pi a^2} \tag{4}$$

The lift force F_l is caused by the shear flow. It can be calculated as follows:

$$F_l = 0.761\frac{\tau_W^{1.5} d_P^3 \rho^{0.5}}{\mu} \tag{5}$$

In Eqs. (4) and (5), $\hbar\varpi$ is the Lifschitz–van der Waals constant (10^{-20} J), d_P the particle size, a the adhesive distance (0.4 nm), τ_W the shear stress, ρ the fluid density and μ the fluid viscosity.

The balance between the adhesion force and the lift force determines whether the particle will be swept off or remain stable on the contact surfaces. The results given in Fig. 4 indicate that the adhesion force is higher than the lift force in a particle diameter range smaller than several microns. This means a small single particle is irreversibly attached to the contact surfaces and only large particles can be removed [26]. So the TS-1 catalyst particles with a mean particle size of 200 nm are easily adhered on the contact surfaces. Because silica particles are several tens of micrometers in diameter, they have a higher lift force in the hydrodynamic conditions of this study, which makes them difficult to deposit on the contact surfaces. When silica particles were added into the reaction system, the scouring effect of suspended silica particles enhanced the shearing stress on the contact surfaces [18], which led to the increase of the lift force of TS-1 particles based on the analysis of Eq. (5). In addition, the collision of silica with deposited

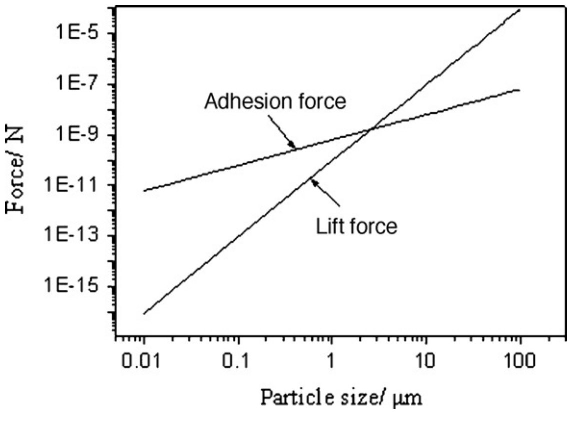


Fig. 4. Estimation of the forces on a particle: fluid density, 800 kg m^{-3}; fluid viscosity, 0.0012 Pa s.

TS-1 provided them enough kinetic energy to overcome adhesion energy between interacting particles. At the same time, the small TS-1 particles could be attached on the surfaces of larger silica particles, which also contributed to the higher catalyst concentration in reaction slurry. As a result, with respect to the system with silica particles, the adhesion of TS-1 catalysts on the contact surfaces can be inhibited and the stable operation time can be increased.

4. Conclusions

In this work, a ceramic membrane reactor system was applied for the continuous acetone ammoximation to acetone oxime over TS-1 catalysts. A method that can improve the operation stability of the membrane reactor system was proposed. Our preliminary research suggests that the addition of microsized silica particles in the system can provide a mechanical scouring effect that removes the already deposited TS-1 away from the contact surfaces and leads to increasing the whole operation efficiency of the system. Meanwhile, the attachment of TS-1 particles on the surfaces of larger silica particles could also contribute to the improvement of the operation efficiency. Being encouraging the results of this explorative study further research is in progress to improve the system performance by optimizing the particle size and concentration of silica and testing other more efficient inert particles able to maintain stable operation for longer time.

Acknowledgments

Financial supports from the National Basic Research Program (2009CB623406), the National Natural Science Foundation (20636020), the Natural Science Foundation of Jiangsu Province (BK2009021) and the Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (09KJB530006) of China are gratefully acknowledged.

References

[1] O. Tahiri Alaoui, Q.T. Nguyen, C. Mbareck, T. Rhlalou, Elaboration and study of poly(vinylidene fluoride)–anatase TiO_2 composite membranes in photocatalytic degradation of dyes, Appl. Catal. A: Gen. 358 (2009) 13–20.

[2] O.M. Ilinich, F.P. Cuperus, L.V. Nosova, E.N. Gribov, Catalytic membrane in reduction of aqueous nitrates: operational principles and catalytic performance, Catal. Today 56 (2000) 137–145.

[3] S. Lee, K. Choo, C. Lee, H. Lee, T. Hyeon, W. Choi, H. Kwon, Use of ultrafiltration membranes for the separation of TiO_2 photocatalysts in drinking water treatment, Ind. Eng. Chem. Res. 40 (2001) 1712–1719.

[4] Y.B. Meng, X. Huang, Q.H. Yang, Y. Qian, N. Kubota, S. Fukunaga, Treatment of polluted fiver water with a photocatalytic slurry reactor using low-pressure mercury lamps coupled with a membrane, Desalination 181 (2005) 121–133.

[5] K. Sopajaree, S.A. Qasimi, S. Basak, K. Rajeshwar, An integrated flow reactor-membrane filtration system for heterogeneous photocatalysis. Part I. Experiments and modeling of a batch-recirculated photoreactor, J. Appl. Electrochem. 29 (1999) 533–539.

[6] C.J. Lu, R.Z. Chen, W.H. Xing, W.Q. Jin, N.P. Xu, A submerged membrane reactor for continuous phenol hydroxylation over TS-1, AIChE J. 54 (2008) 1842–1849.

[7] A. Bódalo, J.L. Gómez, E. Gómez, J. Bastida, M.F. Máximo, M.C. Montiel, Ultrafiltration membrane reactors for enzymatic resolution of amino acids: design model and optimization, Enzyme Microb. Technol. 28 (2001) 355–361.

[8] J. Fu, M. Ji, Z. Wang, L. Jin, D. An, A new submerged membrane photocatalysis reactor (SMPR) for fulvic acid removal using a nano-structured photocatalyst, J. Hazard. Mater. B 131 (2006) 238–242.

[9] I.F.J. Vankelecom, Polymeric membranes in catalytic reactors, Chem. Rev. 102 (2002) 3779–3810.

[10] H.K. Shon, S. Phuntsho, S. Vigneswaran, Effect of photocatalysis on the membrane hybrid system for wastewater treatment, Desalination 225 (2008) 235–248.

[11] A. Trusek-Holownia, Production of protein hydrolysates in an enzymatic membrane reactor, Biochem. Eng. J. 39 (2008) 221–229.

[12] R. Molinari, F. Pirillo, V. Loddo, L. Palmisano, Heterogeneous photocatalytic degradation of pharmaceuticals in water by using polycrystalline TiO_2 and a nanofiltration membrane reactor, Catal. Today 118 (2006) 205–213.

[13] Z.X. Zhong, W.H. Xing, W.Q. Jin, N.P. Xu, Adhesion of nanosized nickel catalysts in the nanocatalysis/UF system, AIChE J. 53 (2007) 1204–1210.

[14] R.Z. Chen, Y. Du, Q.Q. Wang, W.H. Xing, W.Q. Jin, N.P. Xu, Effect of catalyst morphology on the performance of submerged nanocatalysis/membrane filtration system, Ind. Eng. Chem. Res. 48 (2009) 6600–6607.

[15] R.Z. Chen, H.L. Sun, W.H. Xing, W.Q. Jin, N.P. Xu, A submerged ceramic membrane reactor for the *p*-nitrophenol hydrogenation over nano-sized nickel catalysts, J. Nanosci. Nanotechnol. 9 (2009) 1470–1473.

[16] X.H. Liang, Z.T. Mi, Y.Q. Wang, L. Wang, X.W. Zhang, Synthesis of acetone oxime through acetone ammoximation over TS-1, React. Kinet. Catal. Lett. 82 (2004) 333–337.

[17] Y.J. Zhang, Y.Q. Wang, Y.F. Bu, L. Wang, Z.T. Mi, W. Wu, E.Z. Min, S.B. Fu, Z.H. Zhu, Reaction mechanism of the ammoximation of acetone catalyzed by TS-1, React. Kinet. Catal. Lett. 87 (2006) 25–32.

[18] Z.X. Zhong, X. Liu, R.Z. Chen, W.H. Xing, N.P. Xu, Adding microsized silica particles to the catalysis/ultrafiltration system: catalyst dissolution inhibition and flux enhancement, Ind. Eng. Chem. Res. 48 (2009) 4933–4938.

[19] Z.X. Zhong, W.H. Xing, X. Liu, W.Q. Jin, N.P. Xu, Fouling and regeneration of ceramic membranes used in recovering titanium silicalite-1 catalysts, J. Membr. Sci. 301 (2007) 67–75.

[20] G. Petrini, A. Cesana, G. De Alberti, F. Genoni, G. Leofanti, M. Padovan, G. Paparatto, P. Roffia, Deactivation phenomena on Ti–silicalite, Stud. Surf. Sci. Catal. 69 (1991) 761–766.

[21] W.X. Li, W.H. Xing, N.P. Xu, Modeling of relationship between water permeability and microstructure parameters of ceramic membranes, Desalination 192 (2006) 340–345.

[22] Z. Bu, Z.H. Li, R.Z. Chen, W.H. Xing, Optimization of reaction conditions for acetone ammoximation over titanium silicalite-1, J. Nanjing Univ. Technol. 31 (2009) 74–78, (in Chinese).

[23] S. Saxena, J. Basak, N. Hardia, R. Dixit, S. Bhadauria, R. Dwivedi, R. Prasad, A. Soni, G.S. Okram, A. Gupta, Ammoximation of cyclohexanone over nanoporous TS-1 using UHP as an oxidant, Chem. Eng. J. 132 (2007) 61–66.

[24] D. Wang, Z. Liu, F. Liu, X. Ai, X. Zhang, Y. Cao, J. Yu, T. Wu, Y. Bai, T. Li, X. Tang, Fe_2O_3/macroporous resin nanocomposites: some novel highly efficient catalysts for hydroxylation of phenol with H_2O_2, Appl. Catal. A: Gen. 174 (1998) 25–32.

[25] D.L. Pozzo, G. Fornasari, T. Monti, TS-1, catalytic mechanism in cyclohexanone oxime production, Catal. Commun. 3 (2002) 369–375.

[26] J. Altmann, S. Ripperger, Particle deposition and layer formation at the crossflow microfiltration, J. Membr. Sci. 124 (1997) 119–128.