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Intensification of Fast Exothermic Reaction by Gas Agitation in a Microchemical System

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The Beckmann rearrangement of cyclohexanone oxime in oleum as a fast exothermic reaction model is carried out in an adiabatic multiphase microchemical system. A severe coalescene is observed due to the high viscosity of the rearrangement mixture, which decreases the reaction rate and selectivity. Gas agitation is introduced into the microsystem to enhance the reaction by reducing the coalescene and providing an evaporation space to carry away reaction heat. The effects of gas agitation on dispersion performance and mass-transfer rate have been investigated. The acid droplets diameter ranges from about 44 to 20 μm, decreasing with the increase of the gas flow rate. The overall volume mass-transfer coefficient in the microsystem ranges from 0.16 to 0.74 s^{-1}*, 1.5–3.8 times larger than that without gas agitation. The reaction performance is evaluated under different conditions and better conversion and selectivity are obtained.* © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2724–2730, 2014
Keywords: Beckmann rearrangement, ε-caprolactam, gas, microchemical system, mass transfer

Introduction

The classical Beckmann rearrangement, first described more than a century ago,[1] is an important step in the synthesis of ε-caprolactam, the monomer of nylon-6. The industrial process of caprolactam production usually uses benzene or phenol as starting material and consists of three main steps: the synthesis of cyclohexanone, the ammoximation of cyclohexanone to cyclohexanone oxime, and the Beckmann rearrangement of the oxime to ε-caprolactam. For the Beckmann rearrangement step, fuming sulfuric acid (oleum) is mainly used as the solvent and catalyst.[2,3] To obtain caprolactam, large amounts of ammonia have to be used to neutralize sulfuric acid producing ammonium sulfate as by-product. Nearly 2 tons of ammonium sulfate per ton of product is produced in the rearrangement step.[2]

Both the unreacted cyclohexanone oxime and produced caprolactam are dissolved in oleum, forming a viscous “rearrangement mixture.” The viscosity of the mixture is too high to measure with a standard viscosimeter even at 80°C.[4] Besides, as the rearrangement is very rapid and highly exothermic,[5,6] it is difficult to achieve efficient mixing and control the mixture temperature. The hot spot in local area will increase the risk of reactant carbonization and decrease the selectivity. In the industrial process, an external circulation technology is applied for controlling the reaction temperature and enhancing the mixing, which requires quite large reactor volume and long residence time. The residence time in industrial process normally ranges from 15 to 180 min.[7]

Recently, extensive solid acids were used as catalysts both in gas and liquid phase for Beckmann rearrangement of cyclohexanone oxime to avoid the production of ammonium sulfate,[8–14] while low caprolactam selectivity and rapid decay of catalytic activity are mainly encountered during their practical application in the industrial production. Conversely, the microreactor, because of fast mass- and heat-transfer coefficients and good control of residence time, has been applied for intensifying the Beckmann rearrangement.[15–17] In our previous article, high selectivity was achieved when the *M*-ratio ($M\text{-ratio} = ([H_2SO_4] + [SO_3])/[\text{oxime}]$) was around 1.0.[16] At low *M*-ratio, the viscosity of the rearrangement mixture is high and then greatly decreases the heat-transfer coefficient which increases the risk of hot spot. At high *M*-ratio, due to the fast reaction kinetics and large amount of reaction enthalpy ($Q = 254$ kJ/mol),[17] the control of temperature rise is a challenging issue. Therefore, the control of temperature rise still plays a key role in determining the selectivity in a microchemical system.

We can also try to carry on the Beckmann rearrangement in an adiabatic microsystem, which brings several advantages. First, reaction heat could increase the system temperature, decreasing the viscosity of the rearrangement mixture and enhancing the reaction at later period. Second, the high temperature could release more free SO_3 beneficial for reducing the *M*-ratio.[18] Last, the heat exchangers are not needed in the microsystem. However, the control of temperature rise is more challenging. The temperature rise at the adiabatic conditions is about 85°C according to the experimental conditions if the conversion of cyclohexanone oxime is 100%. Also, the severe droplet coalescence,[19] frequently observed in the experiments may decrease the

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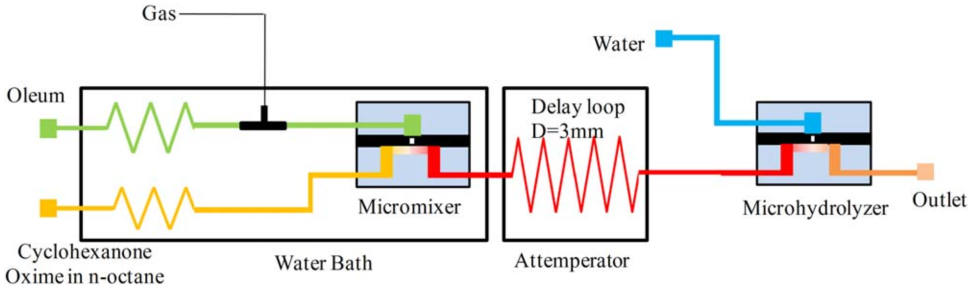

Figure 1. The schematic overview of the experimental setup.

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surface-to-volume ratio, deteriorate the temperature controlling and reaction performance in this adiabatic microsystem.

Gas agitation is an effective method to intensify the interphase transfer in a microchemical system, which has been applied for intensifying solvent extraction processes.[20–22] It can greatly increase the mass-transfer rate by reducing the dispersion scale and intensifying internal circulation flow. For the rearrangement process, the introduction of gas agitation can enhance the heat-transfer rate and also provide an evaporation space in the confined microchannel for the inert solvent to carry away plenty of heat. Furthermore, the gas agitation can reduce the droplet collisions and then increase the interfacial area. In this work, Beckmann rearrangement of cyclohexanone oxime was first carried out in an adiabatic multiphase microchemical system. On the basis of measuring the viscosity of the rearrangement mixture and conducting comparative experiments, we discussed the effect of gas agitation on dispersion performance, mass-transfer rate, and the reaction performance systematically.

Experimental

Materials

Reagents (cyclohexanone oxime and caprolactam) were purchased from J&K Scientific (Beijing). The oleum was provided by Sinopec Group. The organic solvent of octane was of HPLC grade without further purification.

Equipment

The microchemical system consists of a microsieve dispersion mixer, a delay loop and a microhydrolyzer as shown in Figure 1. Cyclohexanone oxime was dissolved in *n*-octane as the continuous phase and oleum as the dispersed phase. In the experiment, cyclohexanone oxime transports from the octane phase to the oleum phase and then the reaction happens in the oleum droplets. The two fluids were delivered by metering pumps (Beijing Satellite Co.) through the pipes immersed in a water bath to control the feeding temperature. To inhibit the precipitation of cyclohexanone oxime in *n*-octane, the feed pipes and the pump head were warmed by self-regulated electric heating bands (Kete electric heating Co.) to keep the temperature at 70°C. Nitrogen gas was introduced into the system before the micromixer by a Tee joint (316 stain steel, the inner diameter of 0.5 mm). The delay loop [polytetrafluoroetylene (PTFE)] with an inner diameter of 1.8 mm and an external diameter of 3 mm was connected directly downstream to the micromixer to control the residence time. The loop was wrapped by thermal insulation material to maintain an adiabatic environment. The reaction time could be controlled accurately by changing the length of the delay loop. The samples were collected at the outlet after the microhydrolyzer.

The micromixer and microhydrolyzer used in the microsystem are microsieve dispersion mixers (316 stainless steel) which are mainly consisted of a distribution chamber and a cross-flow channel. The aperture in the dispersion sheet of the mixer has square shape with 0.2 mm in side length and the cross-flow channel is 12 mm in length, 0.4 mm in width, and 0.6 mm in height. The inner structure of the microhydrolyzer is made of PTFE and there are four microsieves (square shape and 0.4 mm in side length) in the dispersion sheet for water feeding. In the microhydrolyzer, water is added to quench the reaction by hydrolyzing the oleum into sulfuric acid for further analysis.

Analysis

The collected samples were separated into two phases, an organic phase and an aqueous phase. The organic phase was mainly composed of *n*-octane and unreacted cyclohexanone oxime, whereas the aqueous phase of water, caprolactam, cyclohexanone oxime, H_2SO_4, and some undefined byproducts. In the analysis, the two phases were weighed using an electronic analytical balance separately. Then, the organic phase was diluted and measured by GC (HP 6890). The aqueous phase was diluted and neutralized with NaOH solution. Subsequently, the sample was determined by HPLC (Agilent 1100). The cyclohexanone oxime conversion C and caprolactam selectivity S were calculated by the following equations

$$C=1-\frac{W_{\text{org-ox}}\times M_{\text{org}}+W_{\text{aqu-ox}}\times M_{\text{aqu}}}{M_{\text{ox}}} \tag{1}$$

$$S=\frac{W_{\text{org-cap}}\times M_{\text{org}}+W_{\text{aqu-cap}}\times M_{\text{aqu}}}{C\times M_{\text{ox}}} \tag{2}$$

where $W_{\text{org-ox}}$ (%) is the mass fraction of cyclohexanone oxime in the organic phase, $W_{\text{aqu-ox}}$ (%) is the mass fraction of cyclohexanone oxime in the aqueous phase, $W_{\text{org-cap}}$ (%) is the mass fraction of caprolactam in the sample organic phase, $W_{\text{aqu-cap}}$ (%) is the mass fraction of caprolactam in the sample aqueous phase, M_{org} (g) is the mass of the organic phase, M_{aqu} (g) is the mass of the aqueous phase and M_{ox} (g) is the feeding mass of cyclohexanone oxime calculated with the feeding rate of cyclohexanone oxime solution and the sampling time. Most experiments are repeated twice and the average relative errors of replication in conversion and selectivity are 1.3 and 2.4%, respectively.

To understand the effect of gas agitation on the dispersion of oleum, an online observation device was placed just after the micromixer (0.4 m). The device was made of 316

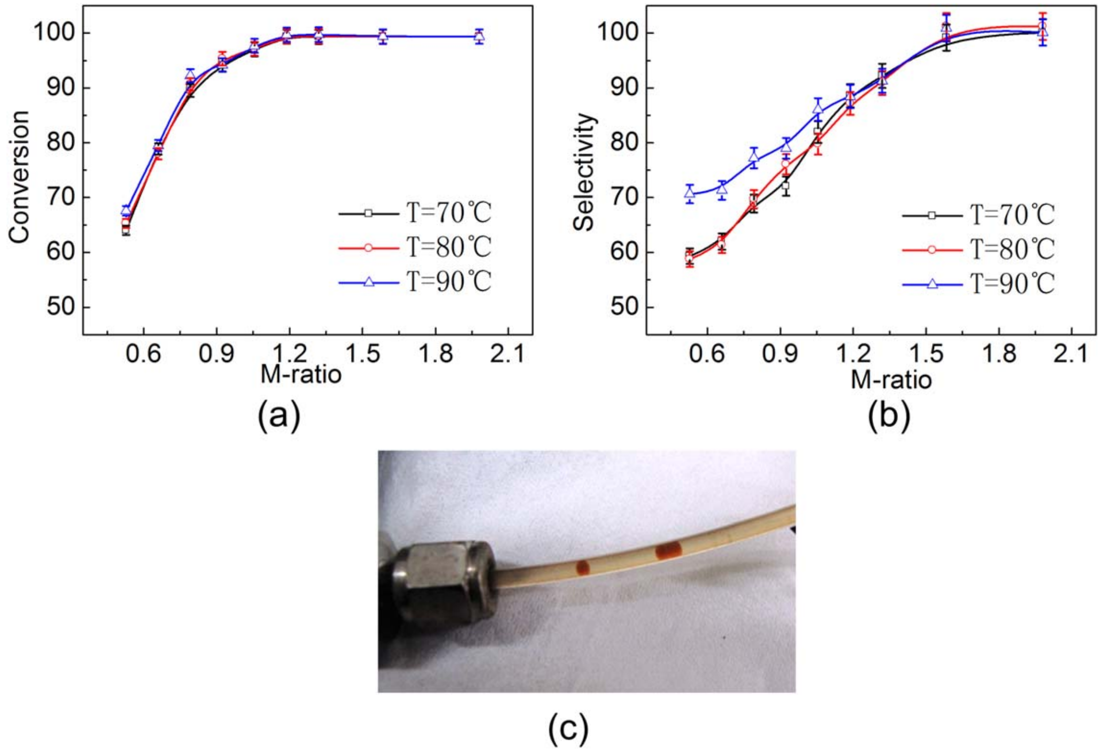

Figure 2. The reaction performance in the adiabatic system.

(a) Effect of *M*-ratio and initial temperature on the conversion of oxime; (b) effect of *M*-ratio and initial temperature on the selectivity to caprolactam; (c) the two-phase flow in the delay loop.

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stainless steel with a slit covered by quartz glass. The slit as the observation window was 30 mm in length, 5 mm in width, and 2 mm in height. A microscope with a CCD video camera (PL-A742, PixeLINK, Canada) was used to record the droplets.

Results and Discussion

The reaction performance in an adiabatic microchemical system without gas introduction

Figures 2a, b show the conversion of cyclohexanone oxime and selectivity to caprolactam at different *M*-ratios with the initial temperature of 70°, 80° and 90°C, respectively. The residence time of reactants in the microsystem is about 46 s to ensure the sufficient conversion. However, nearly 100% conversion is obtained only when *M*-ratio is larger than 1.2. It is also found that the initial temperature can increase the conversion at different *M*-ratios but the amplification is limited. As for the selectivity to caprolactam, it increases with the increase of *M*-ratio and high value of 99+% is obtained when the *M*-ratio is larger than 1.6. The results are quite different from that in our previous results[16] while high selectivity is reached around the *M*-ratio value of 1. The selectivity would become poorer beyond a limited range of around 1.0. Besides, it shows that selectivity increases slightly with the increase of temperature.

The great difference of the reaction performance may result from the coalescence of the viscous rearrangement mixture. In our previous results, the delay loop of the experimental setup is made of steel as a hydrophilic material. If the coalescence of the rearrangement mixture occurs, the mixture would adhere to the inner surface of the delay loop and form an acid film. In this article, the delay loop is made of PTFE with excellent lubricity. The oleum mixture would form plugs as shown in Figure 2c in the delay loop if the coalescence occurs. The decrease of the surface-to-volume ratio here is much larger than the previous one. As a result, the selectivity may decrease at high *M*-ratio due to the extremely high reaction rate in our previous experiments. But in this article, a high *M*-ratio is needed for the complete conversion due to the severe coalescence of the rearrangement mixture. As the reaction kinetics is very fast, it is reasonable that the reaction rate is controlled by the mass-transfer rate between two phases. The mass-transfer rate between two phases is mainly determined by the interfacial area and the convective diffusion. The decreasing of surface-to-volume ratio, due to the increasing of the dispersion scale of oleum, would greatly decrease interfacial area to decrease the mass-transfer rate resulting in long reaction time, and also decrease the interfacial heat-transfer rate to increase the risk of local heat spot in the oleum resulting in low selectivity. The mass-transfer resistance between the two phases is mainly in the octane phase which is not sensitive to the temperature rise. So, the increasing of the reaction rate with the temperature increasing is exact but limited.

As for the selectivity, as all the reactions accelerate with temperature increasing, it cannot establish a simple relationship between the main reaction rate and the selectivity. Herein, we assume that the local heat spots in the oleum have decisive influence, whatever the conversion to caprolactam completes or not. The higher temperature can increase the heat-transfer coefficient in the oleum mixture. It may decrease the local heat spots to prevent from carbonization and then cause the increase of the selectivity. In addition,

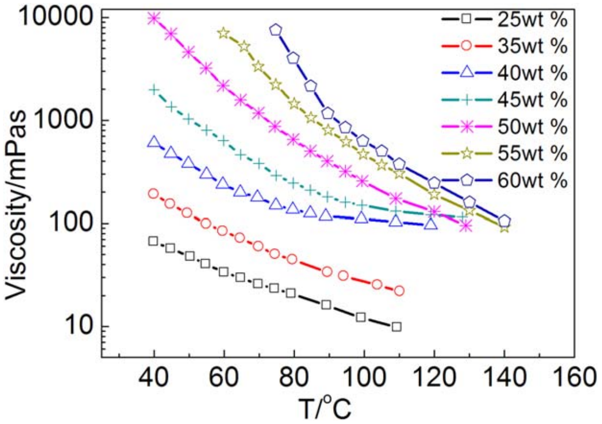

Figure 3. The viscosities of rearrangement mixtures at different caprolactam compositions and temperature.

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the higher temperature may cause more evaporation of octane, which may agitate the system to enhance the heat-transfer further. This may be the reason why higher selectivity was obtained at higher temperature as shown in Figure 2b.

To understand the viscosity change of oleum droplets with the rearrangement reaction proceeding, caprolactam is dissolved in the oleum with different contents and the mixture viscosity is measured by rotational viscometer (DV-II+Pro, Brookfield) at different temperatures as shown in Figure 3. It is clear that the temperature has remarkable influence on the viscosity. With the increase of temperature the viscosity decreases greatly. The facts agree with the previous results that high temperature is beneficial to obtain better reaction performance at the later period. With the increase of caprolactam content in the mixture, the viscosity increases greatly which can reach a high value of 10,000 mPa s even at 80°C (caprolactam composition: 60 wt %). The results mean that the rearrangement mixture viscosity would increase greatly during the rearrangement reaction as the oxime transfers into the oleum. In the end of the reaction, the viscosity would be significantly high at low *M*-ratio. The complete rearrangement mixture contains about 50 wt % of caprolactam when the *M*-ratio is 1.2. The range of the caprolactam content in the rearrangement mixture is 38–69 wt % corresponding to the *M*-ratio of 0.53–1.98 if all the oxime has been converted into caprolactam in the experiments. It can be concluded that the higher temperature at later period is helpful for decreasing the viscosity of the rearrangement mixture, which would reduce the clogging problems and also increase the heat- and mass-transfer rates in the mixture. The results can also help to understand why the reaction is carried out well in an adiabatic system where the system temperature at later period will be increased by reaction heat.

The effect of gas agitation on the dispersion performance

To overcome these problems, gas agitation is proposed to be introduced into the system. Figure 4a shows the flow pattern in the delay loop with the gas agitation (10 mL min^{-1}). We could find that the gas and octane form the gas–liquid slug flow in the delay loop. The oleum is dispersed to small droplets in the octane and separated by the gas slug. The existence of gas could provide an evaporation space in the confined microchannel for the inert solvent to carry away reaction heat. Also, the gas agitation can separate the oleum droplets, reduce the droplet coalescence, and increase the interfacial area. However, we noticed that the oleum mixture still forms plugs in the delay loop as shown in Figure 4b though it has been much smaller than that in Figure 2c. This is probably due to the small gas flow rate (10 mL min^{-1}) compared with the octane flow rate (25 mL min^{-1}). In addition, the oleum droplets dispersed in the octane are so small in the delay loop that they are difficult to be observed clearer by camera without microscope. The dispersion of acid droplets in the octane would be provided in next figure.

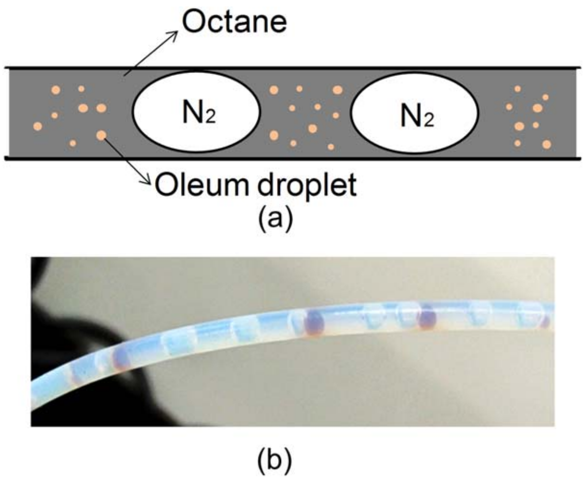

Figure 4. The flow pattern in the delay loop with the gas agitation.

(a) The schematic diagram. (b) The photograph.

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To quantitatively understand the effect of gas agitation on the dispersion performance, octane was used as the continuous phase and sulfuric acid as the dispersed phase during the experiments. The temperature of water bath was kept at 70°C. The online observation device was placed just after the micromixer (0.4 m). The acid droplets were recorded and measured at different operating conditions, as shown in Figure 5. The diameters of sulfuric acid droplets at different gas flow rates were shown in Figure 5a and the microphotographs without or with gas agitation were shown in Figures 5b, c, respectively. We could find that the acid and octane formed dripping flow[23] and the droplet diameter was about 65 μm without gas introduction. When gas phase was introduced into the microsystem, the gas and octane formed the slug flow[20] while the acid was dispersed into the octane as shown in Figure 4a. The results show that the acid was dispersed to smaller droplets (ranging from 20 to 44 μm) with the increase of gas flow rate. It can be concluded that the adding gas can improve the dispersion performance of oleum and decrease the dispersion scale.

The effect of gas agitation on the mass-transfer performance

To evaluate the mass-transfer rate of the microsystem, 3.6 wt % cyclohexanone oxime in octane was used as the continuous phase and sulfuric acid as the dispersed phase. The

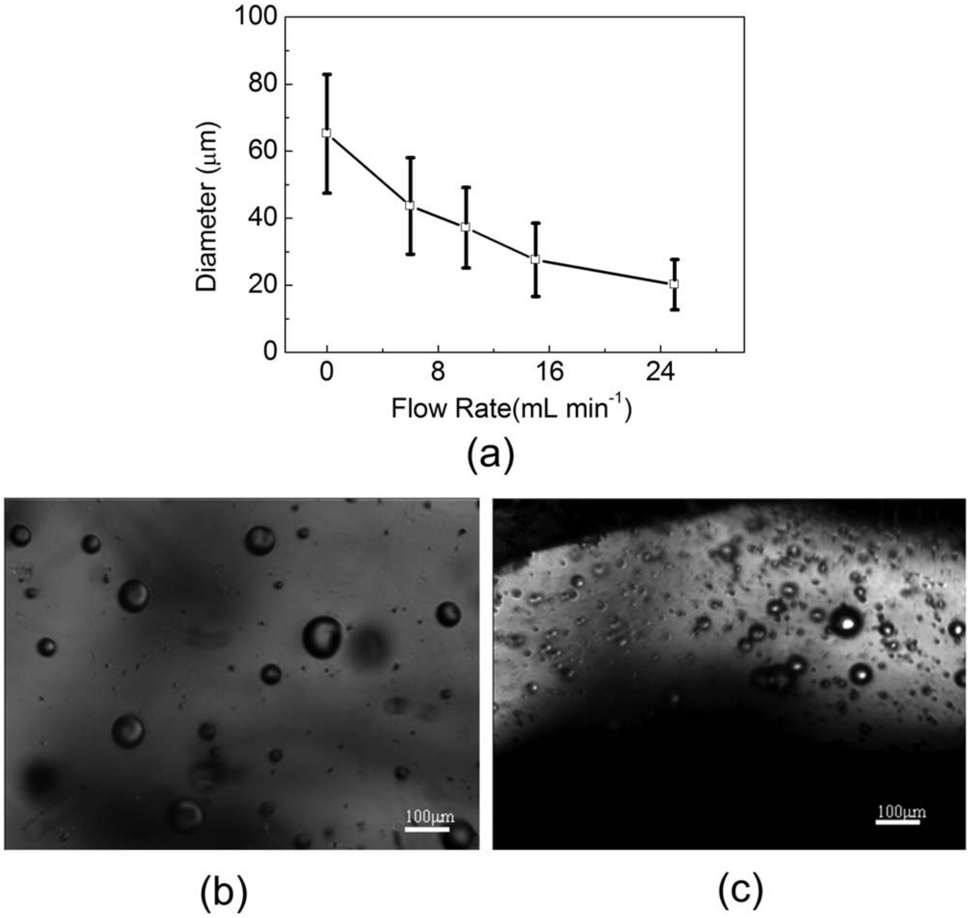


Figure 5. The diameters and microphotographs of sulfuric acid droplets at different operating conditions.

(a) The droplets diameters at different gas flow rates; (b) gas flow rate: 0 mL min^{-1}; (c) gas flow rate: 25 mL min^{-1}. The flow rate of octane was controlled at 25 mL min^{-1} and the flow rates of H_2SO_4 0.8 mL min^{-1}. The length of the delay loop was 0.4 m. The temperature of the water bath was kept constant at 70°C.

temperature of water bath was kept at 70°C. The samples collected just after the micromixer (0.4 m) separated quickly in a test tube (15 mL) and the organic phase was immediately diluted and measured by GC. The oxime concentration in the sulfuric acid phase C_a could also be determined using the overall mass conservation equation. In the experiments, the flow rate ratio of organic phase/acid was kept constant at 31. The gas flow rate was varied from 0 to 25 mL min^{-1}.

From the experimental results, the overall volume mass-transfer coefficient was calculated to evaluate the mass-transfer rate. The mass-transfer rate N can be expressed by Eq. 3

$$N=\frac{\Delta C}{\Delta t}=K_{\mathrm{L}}a\Delta C_{\mathrm{M}} \tag{3}$$

where $K_{\mathrm{L}}a$ is the overall volume mass-transfer coefficient, s^{-1}; ΔC is the concentration difference between sampling concentration and initial concentration, mol L^{-1}; Δt is sampling time, s; C_{M} is the logarithmic mean concentration difference, mol L^{-1}, which is calculated by Eq. 4

$$\Delta C_{\mathrm{M}}=\frac{(C_{\mathrm{o},i}-C^*_{\mathrm{o},i})-(C_{\mathrm{o},0}-C^*_{\mathrm{o},0})}{\ln\left[(C_{\mathrm{o},i}-C^*_{\mathrm{o},i})/(C_{\mathrm{o},0}-C^*_{\mathrm{o},0})\right]} \tag{4}$$

where C_{o} is oxime concentration in the organic phase, mol L^{-1}; C^*_{o} is the equilibrium oxime concentration in the organic phase.

Oxime is slightly soluble in octane but miscible with sulfuric acid. The equilibrium concentration in the octane phase is nearly zero in batch experiments of two contacting liquid phases. As a result, C^*_{o} can assumed to be zero approximately. Equation 4 can be written as

$$\Delta C_{\mathrm{M}}=\frac{C_{\mathrm{o},i}-C_{\mathrm{o},0}}{\ln\left(C_{\mathrm{o},i}/C_{\mathrm{o},0}\right)} \tag{5}$$

Figure 6 shows the overall volume mass-transfer coefficient at different gas flow rates as a function of organic phase flow rate. It is found that the overall volume mass-transfer coefficient ranges from 0.11 to 0.74 s^{-1}, two orders of magnitude higher than that in conventional contactors (1.75–6.3 $\times 10^{-3}$ s^{-1}).[24] For the liquid–liquid flow (without gas introduction), the overall volume mass-transfer coefficient (0.11–0.26 s^{-1}) increases with the increase of organic phase flow rate. This is because that the acid droplet size reduces with the increase of the flow rate and then the interface area increases. Also, the overall mass-transfer coefficient K_{L} can be enhanced by the increase of flow rate. When gas agitation is introduced, the mass-transfer rate (0.16–0.74 s^{-1}) is even higher than that in the liquid–liquid flow as the interface area increases and the internal circulation flow is intensified by the gas agitation. The enhancement factor of gas agitation is about from 1.5 to 3.8. As a result, gas agitation is an effective tool to enhance the mass-transfer performance.

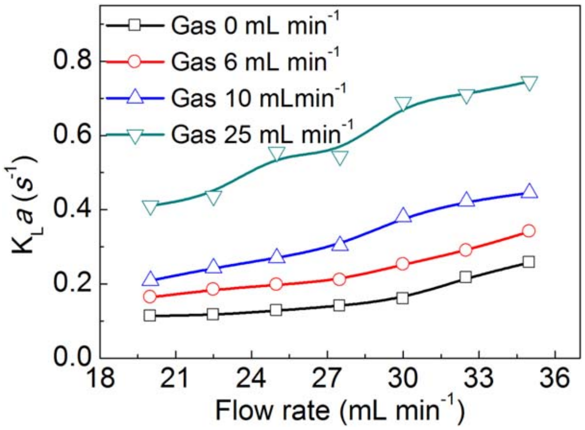


Figure 6. The overall volume mass-transfer coefficients at different gas flow rates as a function of organic phase flow rate.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(a) Without gas

(b) Gas agitation

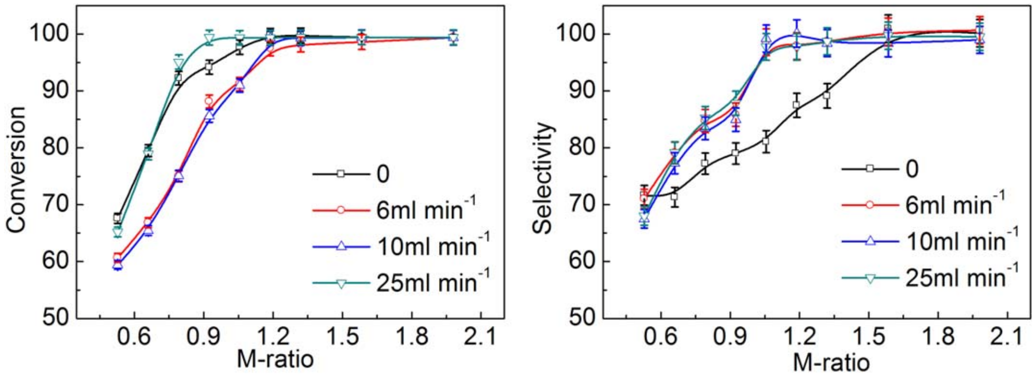
Figure 8. The comparison of samples at different *M*-ratios.

(a) Without gas; (b) gas agitation: 25 mL min^{-1}. Temperature of the water bath was kept at 90°C. Other operating conditions are the same as Figure 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The effect of gas agitation on the reaction performance

Figure 7 shows the conversion of oxime and the selectivity to caprolactam in the microsystem at different gas flow rates as a function of *M*-ratio. As shown in Figure 7a, the conversion for low gas flow rate (6 and 10 mL min^{-1}) is lower than that without gas agitation. There are two main factors affecting the conversion brought by gas agitation. When gas is introduced in the microsytem, it could reduce the coalescence of rearrangement mixture and increases the conversion at a certain residence time. But it could also decrease the residence time. The low conversion at low gas flow rate is probably due to that low gas flow rate performs poor in preventing the coalescence of the rearrangement mixture. The rearrangement mixture still forms plugs in the delay loop as shown in Figure 4b. Meanwhile, the addition of gas reduces the reaction time. As a result, lower conversion is obtained when less gas is introduced into the microsystem. When gas flow rate is increased to 25 mL min^{-1}, nearly 100% conversion could be obtained when the *M*-ration is as low as 0.9. Considering the reaction time has been reduced from about 46 to 23 s, the improvement is quite remarkable. The results indicate that only introducing enough gas can prevent the coalescence of rearrangement mixture and enhance the reaction simultaneously.

As for the selectivity, we can find that the gas agitation is beneficial to improve the selectivity as shown in Figure 7b. A high selectivity of above 97% could be obtained when the *M*-ratio is larger than 1.05. In our previous studies,[16] an optimized range of *M*-ratio around 1.0 exists for the rearrangement in the microsytem. At low *M*-ratio, some by-products, such as octahydrophenazine and cyclohexanone, would increase and also local heat spot would arise due to the sharply increased viscosity. At high *M*-ratio, the reaction rate is so fast that the hard-to-control temperature increases the risk of reactant carbonization. The introduction of gas agitation can increase the interface area and intensify the internal circulation flow, resulting in intensifying the heat transfer vigorously. Also, the gas provides an evaporation space in the confined microchannel for the inert solvent to carry away reaction heat. As a result, the side reaction of carbonization could be greatly reduced.



(a) (b)

Figure 7. The reaction performance in the microsystem by introducing gas agitation.

(a) Effect of *M*-ratio and gas flow rate on the conversion of oxime; (b) effect of *M*-ratio and gas flow rate on the selectivity to caprolactam. Temperature of the water bath was kept at 90°C. Other operating conditions are the same as Figure 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 shows the collected samples photographs at different M-ratios. From left to right, the M-ratios decrease from about 1.98 to 0.66 corresponding to the conditions shown in Figure 7. The results shown in Figure 8a correspond to those in Figure 2b at 90°C. The results shown in Figure 8b correspond to those in Figure 7b with the gas flow rate of 25 mL min^{-1}. We can find that without gas agitation the sample color grows darker with the decrease of M-ratio, indicating the greatly increased side reaction of carbonization. When the gas agitation is introduced, all the samples are nearly transparent. The results give an intuitive verification that the temperature is well controlled in the adiabatic system.

In a word, the introduction of gas agitation is found to be an efficient way to intensify the mass- and heat-transfer rate in the adiabatic microsytem. By a sufficient gas agitation to prevent the coalescence of oleum droplets, the reaction rate increases greatly, achieving high selectivity, compared to the process without gas agitation. Besides, the rise of temperature can be easily controlled and the safety is improved. As a result, the introduction of gas is very useful for reliable design of Beckmann rearrangement processes.

Conclusions

In this work, gas agitation was introduced to the adiabatic microsystem to enhance the fast exothermic reaction of Beckmann rearrangement successfully. The addition of gas could improve the dispersion performance of oleum and the acid could be dispersed to smaller droplets (ranging from 20 to 44 μm). Both the mass transfer and reaction performance were evaluated, as well as the effects of gas flow rate and M-ratio. The overall volume mass-transfer coefficient in the microsystem ranged from 0.16 to 0.74 s^{-1}, 1.5–3.8 times larger than that without gas agitation. Reaction rate was found to be remarkably increased as the gas agitation was sufficient to prevent the coalescence of rearrangement mixture. However, the selectivity was greatly improved corresponding to less side reaction of carbonization with gas agitation. The introduction of gas agitation provides an effective way to improve the safety and make reliable design of Beckmann rearrangement processes.

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