Journal of Flow Chemistry (2024) 14:529–537
https://doi.org/10.1007/s41981-024-00324-1

FULL PAPER

Efficient pinnick oxidation by a superheated micro-reaction process

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Received: 11 January 2024 / Accepted: 6 March 2024 / Published online: 20 March 2024

Abstract

The Pinnick oxidation, due to its tolerance for sensitive functional groups, is widely used in the process of oxidizing α,β-unsaturated aldehydes to corresponding carboxylic acids. The reaction reagents typically include sodium chlorite, buffer salts, and a scavenger. However, the controllability of Pinnick oxidation in the batch reaction process is poor due to the inherent limitations of the reactor's performance. This leads to potential safety risks and necessitates the reaction to proceed slowly under conditions of low temperature and low concentration. In this work, we introduced a new continuous micro-reaction process to intensify the Pinnick oxidation. The water-soluble crotonic acid was selected as a typical object of study. Through the study of reaction parameters and the construction of a micro-reaction system, efficient continuous process was achieved under high-temperature and high-pressure conditions for the first time. Compared to the batch process, the reaction benefited from the superheated condition resulting in a significant acceleration of the reaction rate, efficient gas–liquid interphase mass transfer allowing for effective utilization of the generated chlorine dioxide, and the inherent safety of the microreactor enabling an increase in reaction concentration. In addition, the buffer salts used in the Pinnick oxidation has been successfully replaced by hydrochloric acid and applied to the continuous flow. This work shows the tremendous potential of microreactors in utilizing harsh reaction conditions to achieve process intensification.

Article Highlights

- A superheated micro-reaction process was introduced into the Pinnick oxidation to achieve efficient and safe preparation of crotonic acid.
- Efficient gas–liquid interphase mass transfer in microreactor realized effective utilization of the by-product chlorine dioxide.
- The great replacement of phosphate buffer salts with hydrochloric acid was achieved in continuous flow.

Keywords Microreactor · Oxidation · Continuous synthesis · Pinnick oxidation · Process intensification

Introduction

The Pinnick oxidation is commonly used for the conversion of aldehydes to their corresponding carboxylic acids by using sodium chlorite, mild acidic condition, and a scavenger [1–3]. There exist kinds of methods to oxidize aldehydes, such as $KMnO_4$, H_5IO_6, CrO_3, $KHSO_5$, etc. [4–9], but only a few are amenable to a broad range of functional groups. The Pinnick oxidation has proven to be both tolerant of sensitive functional groups and capable of reacting with sterically hindered groups. Additionally, the reagents used are relatively inexpensive. Molecular oxygen is currently considered to be a clean and sustainable oxidant for oxidation reactions, and it possesses a unique advantage over the

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other oxidants in that it produces water as the byproduct with a high atom economy. However, despite significant progress in aerobic oxidation of aldehydes [10–13], it still faces the challenges of limited substrate applicability and harsh conditions. In addition, there are issues such as the slow reaction rate resulting from gas–liquid mass transfer, the relatively low conversion rate caused by product inhibition [14], and limited selectivity due to rearrangement of Criegee intermediate [15–17]. Hence, within many organic synthesis routes, the Pinnick oxidation method remains a favored option for the oxidation of aldehydes, especially for α,β-unsaturated aldehydes [18–23].

The proposed reaction mechanism of Pinnick oxidation involves chlorous acid as the active oxidant, which is formed under acidic conditions from sodium chlorite [24]. First, the chlorous acid adds to the aldehyde to form a five membered ring. Then resulting structure undergoes a pericyclic fragmentation in which the aldehyde hydrogen is transferred to one oxygen on the chlorine, with the chlorine group releases as a byproduct, hypochlorous acid. The hypochlorous acid is a reactive oxidizing agent which can cause undesired side reactions such as consumption of the sodium chlorite to form chlorine oxide or reacting with C = C double bonds (Fig. 1). A scavenger must be added to the reaction to consume the formed hypochlorous acid. 2-Methyl-2-butene, resorcinol, sulfamic acid and hydrogen peroxide are common scavenger reagents [25, 26]. Comparing these scavengers, the Pinnick oxidation with hydrogen peroxide has cost advantages and simpler post-processing. However, there are still some problems that need to be addressed for this reaction

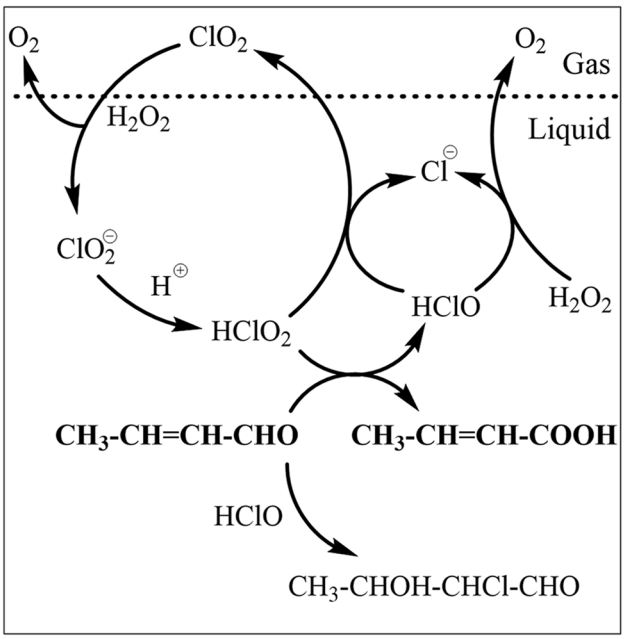

Fig. 1 Proposed mechanism for the Pinnick oxidation

system to be used in practical production. 1) Chlorous acid is unstable and undergoes thermal decomposition to produce explosive gas chlorine dioxide. Due to the high density of chlorine dioxide, it easily accumulates in gas phase, posing a safety hazard. Considering the poor controllability of the batch process, the reaction usually proceeds slowly at low temperatures (≤ 25 °C) with low concentrations (≤ 0.3 mol/L), resulting in low reaction efficiency. 2) The reaction generates oxygen of equal equivalence, making it difficult for normal batch reactors to handle. Therefore, the laboratories prefer to use 2-methyl-2-butene as the HOCl scavenger [18, 21, 22]. 3) The Pinnick oxidation typically requires large amounts of phosphate buffer salts (> 1 equiv.), causing high post-processing costs. 4) Existing literature indicates that this reaction performs worse in aliphatic α,β-unsaturated or more hydrophilic aldehydes, such as crotonaldehyde [25].

Micro-reaction technology, with its efficient heat and mass transfer performance and inherent safety, can effectively broaden the reaction operation window and handle well with harsh reaction conditions such as high temperature, high pressure, and high concentration [27–30]. The superheated micro-reaction process is extensively employed for process intensification of chemical synthesis, including adipic acid, 2-arylbenzazoles, 2-allylphenol and ε-caprolactam [31–33]. In our previous work, with the advantages of faster mixing of miscible phases and improved heat transport of the microreactor, Hoffman rearrangement was completed continuously and efficiently through a simple one-step high-temperature reaction [34, 35]. In an integrated batch – DIY flow system, Burkart et al. realized the Pinnick oxidation in microreactor at normal temperature and pressure. However, this micro-reaction process did not fully utilize the performance advantages of the microreactors, and had problems such as a relatively long residence time (20 min) and high consumption of sodium chlorite (2 equiv.) [36].

This work aimed to develop a new continuous process for Pinnick oxidation using micro-reaction technology, effectively solving the problems of low production efficiency in the existing batch synthesis process, improving process controllability and safety. We selected the water-soluble crotonic acid as a typical object of study. Crotonic acid, as a short carbon chain α,β-unsaturated fatty acid, has a wide range of applications in functional materials and the pharmaceutical field. Initially, we investigated the influence of various parameters (temperature, reagent dosage and pH) on the reaction. However, due to the limitations of the batch equipment performance and the potential safety risks, it was not feasible to further intensify the reaction through harsh reaction conditions. By introducing a micro-reaction system, efficient continuous reaction process was achieved under high-temperature and high-pressure conditions.

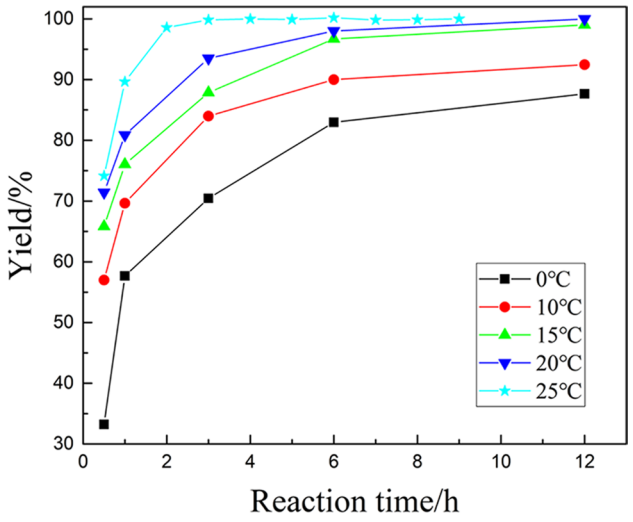

Fig. 2 Influence of reaction temperature on the yield. Reaction conditions: *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/$NaClO_2$/H_2O_2/H_3PO_4/NaH_2PO_4 = 1:1.4:2:0.35:0.65(mole)

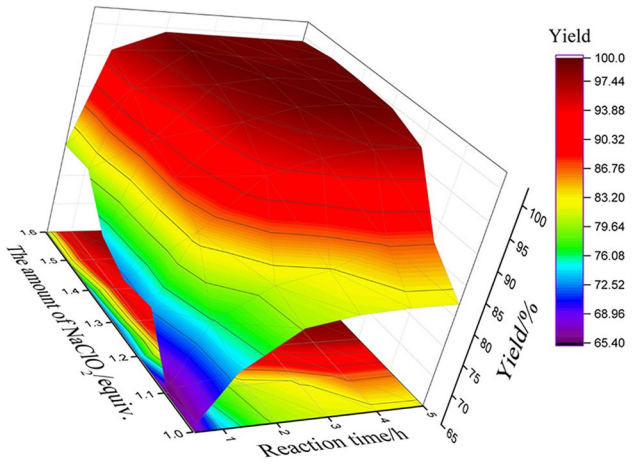

Fig. 3 Influence of the amount of $NaClO_2$ on the yield. Reaction conditions: 25 °C, *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/H_2O_2/H_3PO_4/NaH_2PO_4 = 1:2:0.35:0.65(mole)

Compared to the batch process, the reaction benefited from an increased temperature resulting in a significant acceleration of the reaction rate, efficient gas–liquid interphase mass transfer allowing for effective utilization of the by-product chlorine dioxide, and the inherent safety of the microreactor enabling an increase in reaction concentration. In addition, the buffer salts used in the Pinnick oxidation has been successfully replaced by hydrochloric acid.

Results and discussion

Effects of reaction temperature

The reaction temperature plays the dominant role due to its nonlinear impact on the reaction rate and consequent heat release rate. In consideration of safety, the effect of temperature, ranging from 0 to 25 °C, on the reaction was examined in the batch reactor. As shown in Fig. 2, a notable acceleration in the reaction rate was observed with the increase of reaction temperature. Remarkably, at 25 °C, another reaction time of 3 h after addition of $NaClO_2$ was able to achieve a complete conversion of crotonaldehyde with almost 100% yield. An intriguing experimental observation was the generation of a greater volume of yellow-green gas, and a consequent darkening of the gas phase, with the rise in temperature (Figure S1). The main component of this yellow-green gas was presumed to be ClO_2, originating from the decomposition of $HClO_2$ or the reaction between HClO and $HClO_2$. The decomposition of $HClO_2$ was markedly accelerated by the increase in reaction temperature. Given the significantly higher density of ClO_2 compared to oxygen or air, it tended to accumulate near the liquid surface, thereby posing huge safety risks. While ClO_2 is typically safe in aqueous solutions, it is generally believed that the lower concentration limit for the explosion of ClO_2 gas in the gas phase is approximately 10 vol% [37]. Hence, in the literature when using the batch process for Pinnick oxidation, the reaction temperature was typically maintained below room temperature, and the concentration of reactants was kept low to prevent temperature runaway.

Effects of the amount of reaction reagents

Sodium chlorite, acting as the principal oxidizing agent, holds significant importance for the reaction rate. It can be seen from Fig. 3 that with the increase of the amount of $NaClO_2$, there was a significant increase in reaction rate and final yield. The necessity for an excessive amount of $HClO_2$ was primarily attributed to its propensity for decomposition, and a portion of $HClO_2$ was consumed by HClO. Owing to the poor gas–liquid mass transfer capability of the traditional batch reactor, the gaseous ClO_2 was almost incapable of being reabsorbed back into the reaction solution for reuse. Under such conditions, about 1.3 equiv. of $NaClO_2$ was required to achieve a complete conversion of crotonaldehyde.

The main function of hydrogen peroxide is to timely scavenge the byproduct, HClO, thereby avoiding its reaction with $HClO_2$ which results in the consumption of $NaClO_2$. Meanwhile, it has been proved that HClO directly interacts with the crotonaldehyde, leading to a reduction in selectivity. As illustrated in Fig. 4, in the absence of H_2O_2, the yield and selectivity of the reaction

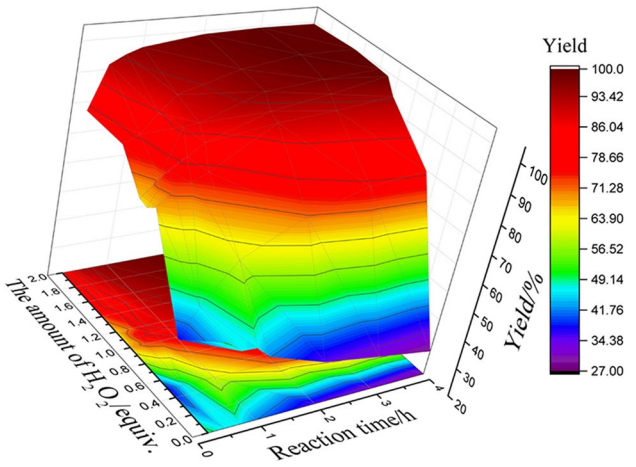

Fig. 4 Influence of the amount of H_2O_2 on the yield. Reaction conditions: 25 °C, *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/$NaClO_2$/H_3PO_4/NaH_2PO_4 = 1:1.4:0.35:0.65(mole)

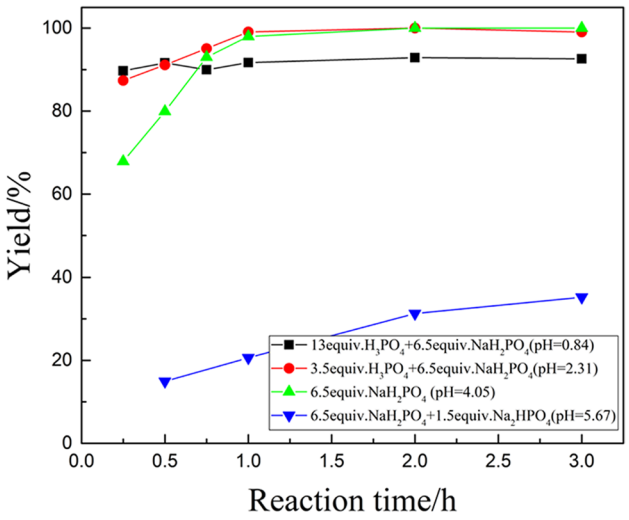

Fig. 5 Influence of the composition of buffer salts on the yield. Reaction conditions: 25 °C, *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/$NaClO_2$/H_2O_2 = 1:1.4:2(mole)

began to significantly decline after 15 min. When the equivalent of H_2O_2 reached 1.1 or more, the reaction selectivity can attain 100%. Excess H_2O_2 helped to accelerate the reduction of HClO. The increase in the amount of H_2O_2 also greatly helped to improve the reaction rate. By oxidizing HClO to HCl more quickly, the concentration of hydrogen ions in the solution can be increased, thereby converting more hypochlorous acid ions into the actual oxidant, $HClO_2$.

Effects of pH

The pH determines the concentration of $HClO_2$ molecules, which has a direct impact on the reaction rate. The advantage of a lower pH was that it fostered the thermal stability of H_2O_2 and expedited the reaction between H_2O_2 and HClO. However, a higher concentration of $HClO_2$ molecules in the solution aggravated its self-decomposition, leading to a decrease in the utilization rate of $NaClO_2$. Therefore, phosphate buffer salts were typically employed in batch process to regulate the reaction under suitable acidic conditions. A study of the effect of buffer systems with different pH values on the reaction revealed that as the pH decreased, the reaction rate significantly increased (Fig. 5). For example, when the reaction time was 0.5 h, the conversion rate at pH = 2.31 exceeded 90%, while at pH = 5.67, it was only 20%. When the pH was 0.84, an obvious decline in reaction selectivity was observed. The primary reason as confirmed was that crotonaldehyde exhibited instability and was susceptible to spoilage under strongly acidic conditions (Figure S2). Above all, a moderate pH environment was of paramount importance for the Pinnick oxidation.

When using buffer salts, the issue of buffer capacity must be considered. As can be seen from the main reaction equation (Eq. 1), the primary influence on pH was the generation of additional organic weak acids (pKa = 4.69 at 25 °C). Although the formation of this weak acid caused a decrease in the pH of the reaction solution, the extent of the decrease was limited. It would not lower the pH to a very low level, such as below 1.5, which caused the crotonaldehyde to deteriorate.

$$RCHO + HClO_2 + H_2O_2 \rightarrow RCOOH + HCl + H_2O + O_2 \uparrow \quad (1)$$

There were also other factors that influenced the pH of the reaction solution. The $NaClO_2$ (Adamas, 80%) utilized contained minor quantities of sodium hydroxide and sodium carbonate. Acid–base titration determined the content of these two alkalis to be 0.52% and 0.66% respectively. Upon calculation, the corresponding acid requirement was 0.03 times the amount of $NaClO_2$. From the combination of hydrogen ions with aldehydes, to their eventual release back into the solution through the reduction of HClO, there existed a certain time lag. During this period, the presence of buffering salts was crucial to maintain an appropriate pH range. In Fig. 6, it was observed that as the buffer capacity decreased, the reaction rate significantly decreased. The introduction of $NaClO_2$ led to an increase in pH at the beginning due to the presence of alkaline substances. Systems with a high buffer capacity, which can maintain a lower pH range, had more hydrogen ions available for the reaction. By monitoring the pH changes during the reaction, it was noted that the pH gradually increased as the reaction progressed. This was attributed to the formation of the weak organic acid and the release of the used hydrogen ions.

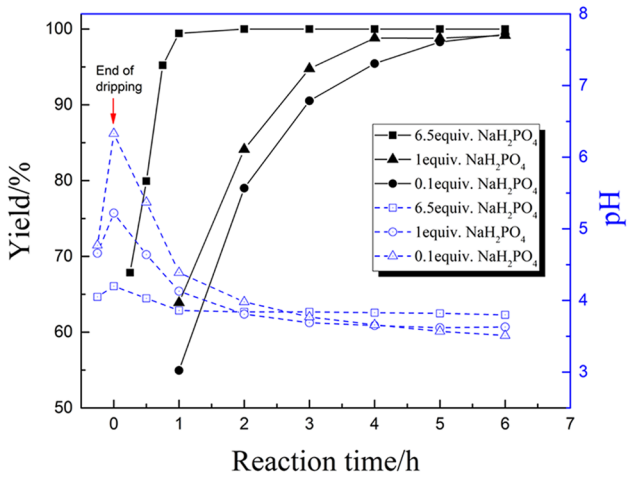

Fig. 6 Different buffer capacities (left) influence on the reaction rate; (right) pH change during the reaction process. Reaction conditions: 25 °C, *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/$NaClO_2$/H_2O_2 = 1:1.4:2(mole)

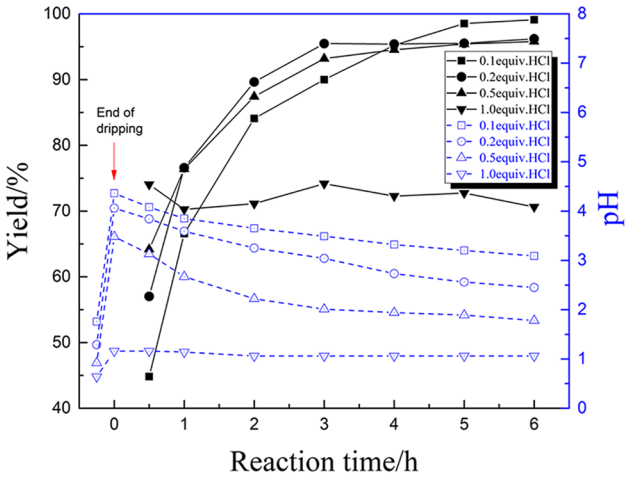

Fig. 7 Different additive amounts of HCl (left) influence on the reaction rate and yield; (right) pH change during the reaction process. Reaction conditions: 25 °C, *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/$NaClO_2$/H_2O_2 = 1:1.4:2(mole)

From a production process perspective, the use of phosphate buffer system not only increases the cost of reagents, but also complicates the treatment of subsequent waste liquids. Therefore, it is worth contemplating how to avoid the use of phosphate buffer system. For this reaction, when the pH was high, the reaction rate slowed down, and when the pH was too low, the raw materials were prone to deterioration. Moreover, as the reaction progressed, the pH tended to decrease. Despite these challenges, we believed that there was a certain feasibility in using traditional inorganic strong acids (e.g., HCl) to replace the phosphate buffer system. By studying the effects of different amounts of HCl (Fig. 7) on reaction, it can be observed that the reaction can proceed smoothly even without the use of a phosphate buffer system. The more HCl was used, the faster the reaction proceeded. As expected, adding too much acid would lead to a decrease in selectivity. It's worth mentioning that in the batch reactor, rapid feeding may lead to uncontrolled reactions, rapid generation of oxygen, and difficult operation, particularly in large-scale production. A slower material addition speed and poorer mixing uniformity can easily lead to a momentary high local acid concentration. Especially when the reaction concentration was high, the acid needed to neutralize sodium hypochlorite may be greater than the acid needed to adjust the pH. Therefore, a faster mixing method was needed to reduce the deterioration of raw materials by inorganic acids.

Process intensification by microreactor

In the optimization of the batch process, we encountered many difficulties in safety, gas–liquid mass transfer efficiency, process controllability, and rapid mixing. Next, we aimed to broaden the operational scope and intensify the reaction process by utilizing the microreactor.

Firstly, we increased the system pressure to prevent solvent boiling and reagent decomposition at high temperature. Simultaneously, high system pressure minimized the impact of gas generation, which significantly reduced the residence time in the microreactor. From the Fig. 8, as the reaction temperature increased, the reaction rate significantly increased. Surprisingly, the reaction selectivity can consistently be maintained close to 100%. For the side reactions that may happen at high temperature, it was observed from Figure S3 that the crotonaldehyde underwent self-polymerization under high temperature conditions, leading to a rapid decrease in the concentration. After heating reflux reaction of the normal pressure in batch reactor was over, there were noticeable oil-like polymer impurities generated on the wall (Figure S4). In the microchannel, on one hand, the consumption speed of the raw materials greatly increased. On the other hand, due to the continuous high-intensity gas–liquid two-phase mixing, oxygen, acting as a coagulant, can effectively inhibit the self-polymerization of the crotonaldehyde. Therefore, the method of using high-temperature superheated flow process for reaction intensification was feasible. For the subsequent experiments, the continuous reaction conditions at 120 °C and 4 MPa were chosen.

Hydrogen peroxide is relatively stable under acidic conditions and does not decompose significantly over a short period. Therefore, the utilization rate of H_2O_2 under high-temperature and high-pressure conditions remained high (Fig. 9), essentially consistent with the conditions in low-temperature batch process.

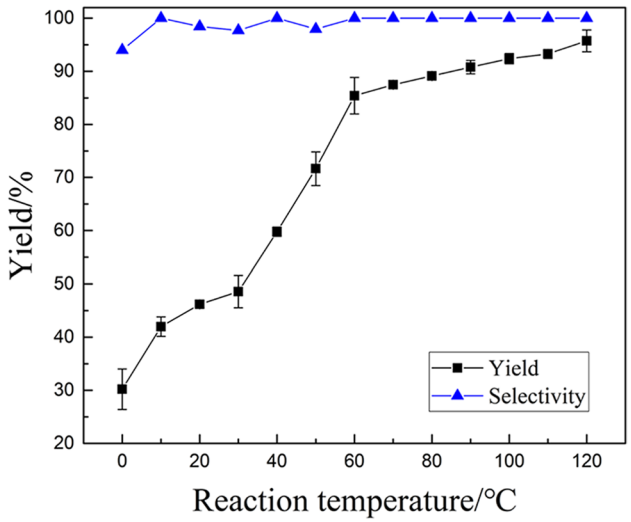

Fig. 8 Influence of reaction temperature on the yield in the micro-reactor. Reaction conditions: 4.0 MPa, residence time = 1.5 min, *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/$NaClO_2$/H_2O_2/H_3PO_4/NaH_2PO_4 = 1:1.4:2.4:0.35:0.65(mole)

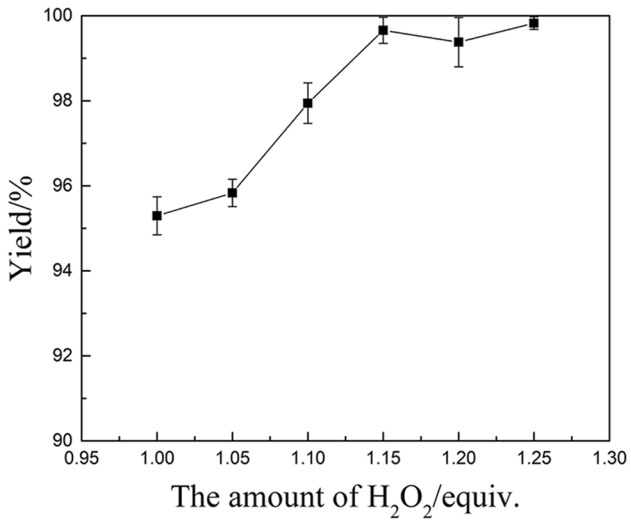

Fig. 9 Influence of the amount of H_2O_2 on the yield in the high-temperature and high-pressure micro-reaction process. Reaction conditions: 120 °C, 4.0 MPa, residence time = 5 min, *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/$NaClO_2$/H_3PO_4/NaH_2PO_4 = 1:1.4:0.35:0.65(mole)

Considering the increase in temperature, the decomposition of chloric acid certainly intensified. Surprisingly, high-temperature superheated flow process required less $NaClO_2$, not more (Fig. 10). This suggested that in microchannels, due to the higher gas–liquid mass transfer coefficient, ClO_2 generated by side reactions can be effectively reabsorbed and reused through reactions with H_2O_2. Moreover, at the microscale, gravity no

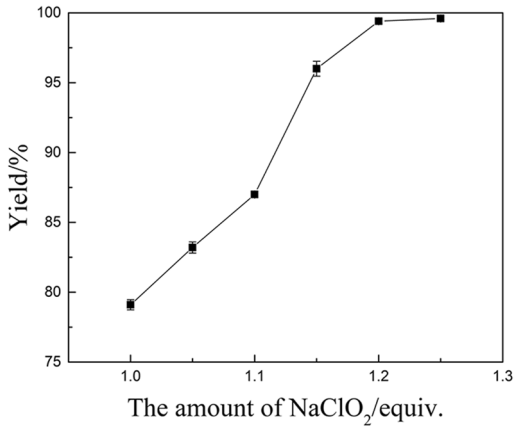

Fig. 10 Influence of the amount of $NaClO_2$ on the yield in the high-temperature and high-pressure micro-reaction process. Reaction conditions: 120 °C, 4.0 MPa, residence time = 6 min, *c*(crotonaldehyde) in mixture = 0.1 mol/L, crotonaldehyde/H_2O_2/H_3PO_4/NaH_2PO_4 = 1:1.2:0.35:0.65(mole)

longer played a dominant role, and there was no local enrichment of ClO_2 in the gas phase. The equivalent oxygen generated timely diluted the concentration of ClO_2 in the gas phase, making the actual gas phase concentration of ClO_2 far below the lower concentration of the explosion limit, which effectively ensured the safety of the continuous process.

We also adjusted the amount of HCl for the reaction with 1.2 equiv. $NaClO_2$ and 1.1 equiv. H_2O_2. Insufficient HCl can slow down the reaction rate, making it difficult to complete the reaction quickly in flow. The continuous process can achieve instantaneous mixing of multiple streams, allowing the use of higher concentrations of HCl without worrying about the deterioration of raw materials due to untimely mixing leading to locally high acidity. This was difficult to achieve in the batch process through dropwise addition. As can be seen from the Fig. 11, when high-temperature and high-pressure continuous conditions were employed, the reaction time can be shortened from several hours to just a few minutes. It's worth noting that the optimal amount of HCl may vary depending on the concentration of the reactants. That is because the acid was used in part to neutralize the sodium carbonate and sodium hydroxide contained in $NaClO_2$, and in part to provide the acidic environment required for the reaction. The higher the concentration of the reaction, theoretically, the less the equivalent of HCl required. At a raw material concentration of 0.6 mol/L, the use of 0.1 equiv. HCl can achieve a yield of 99% in 3 min.

To further exemplify the utility and safety of the high-temperature and high-pressure micro-reaction process, a multi-gram scale experiment was carried out by employing 0.2 mol (14 g) of crotonaldehyde with the reaction

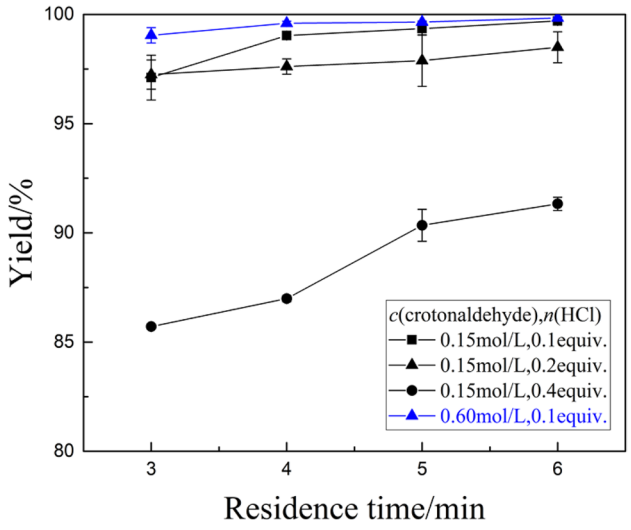

Fig. 11 Reaction effects under different reactant concentrations in the high-temperature and high-pressure micro-reaction process. Reaction conditions: 120 °C, 4.0 MPa, crotonaldehyde/$NaClO_2$/H_2O_2 = 1:1.2:1.1(mole)

concentration of 0.6 mol/L. In the presence of 1.2 equiv. $NaClO_2$, 1.1 equiv. H_2O_2 and 0.1 equiv. HCl, the Pinnick oxidation proceeded smoothly to provide the desired product crotonic acid in 95.6% isolated yield with 98.1% purity.

Conclusions

In summary, we have developed an efficient and continuous micro-reaction system for Pinnick oxidation. Through the batch reaction system, we studied the influence of factors such as temperature, reagent equivalents, and pH. We found that due to the performance and safety of the equipment, the batch reaction can only achieve good results under low concentration, low temperature, and slow reaction rate. However, with the help of the microreactor, we broke this limitation, realized overheating micro-reaction process. Efficient gas–liquid mass transfer has enabled the reuse of the byproduct chlorine dioxide, improving the utilization rate of the oxidant sodium hypochlorite under high temperatures. Through the rapid mixing of multiple streams of reactants, we have achieved the great replacement of phosphate buffer salts with hydrochloric acid in continuous flow process. The inherent safety and controllability of the microreactor enabled an increase in reaction concentration and reaction rate. Ultimately, at 0.6 mol/L, a residence time of 3 min in microchannel at 120 °C and 4.0 MPa was employed to produce crotonic acid in 95.6% isolated yield with relatively low reagent consumption.

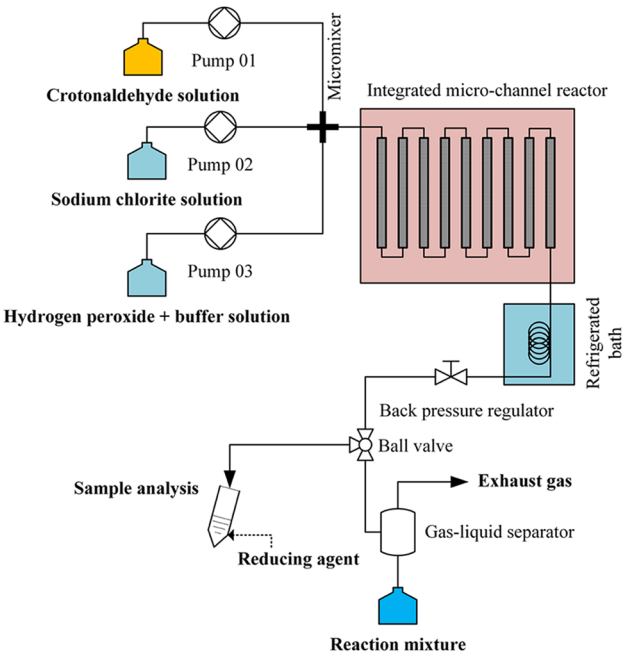

Fig. 12 Schematic of the microreaction system

Materials and methods

Materials

Crotonaldehyde (Adamas, 99%), crotonic acid (adamas, 98%), sodium chlorite (Adamas, 80%), hydrogen peroxide (Greagent, 30%), sodium ascorbate (Adamas, 99%), acetonitrile (Adamas, 99.9%), sodium dihydrogenorthophosphate (Greagent, 99%), sodium phosphate dibasic (Greagent, 99%), hydrochloric acid (Greagent, 36–38%), methyl tert-butyl ether (Adamas, 99%) were purchased from *Tansoole*. All reagents were not further purified before use.

Continuous reaction process

As shown in Fig. 12, the reactants were divided into three feed solutions, acetonitrile containing crotonaldehyde, H_2O_2 solution containing phosphate buffer salts, and $NaClO_2$ aqueous solution. Three feed solutions were delivered to the system respectively by high-pressure plunger pumps (SZWEICO, 2PB3020IV). Here, we used a simple cross-shaped micromixer (the inner diameter of 0.25 mm) to realize rapid mixing of three feed solutions. Subsequently, the mixed fluid was carried to a printed micro-channel reactor (HZSS, WRC00820, Ti) for further reaction. The printed micro-channel reactor achieves efficient heat transfer with a heat transfer coefficient of up to 1500 W/(m^2·K). The residence time can be adjusted by changing the number of series reactors (the internal volume of each reactor is 8.2 ml) or the total flow rate. As for the impact of gas generation on

residence time, it was calculated that the deviation was less than 10% at a pressure of 4 MPa and low reactant concentration (0.1 mol/L). The residence time at high concentrations can be modified using the following equation:

$$t = \frac{V}{F(1 + c\eta RT/2p)} \quad (2)$$

where t is the residence time; V is the reactor volume; F is the total flow rate; c is the concentration of crotonaldehyde; η is the reaction conversion. A cooling unit was arranged at the outlet of the micro-channel reactor to quench the reaction. A back pressure regulator was used to control the system pressure. The reaction solution was separated continuously by a gas–liquid separator to obtain the desired aqueous phase. Unreacted oxidants in aqueous phase were destroyed by Na_2SO_3, and acetonitrile was removed by evaporation. Finally, the residual solution was extracted 3 times with equal volume of methyl tert-butyl ether, and the crude product was collected by removal of organic solvent. In the experiment, rapid sampling can be achieved using a three-way valve, and the reaction conversion rate and yield can be obtained by HPLC detection of the aqueous reaction solution (acetophenone was selected as the internal standard). Considering that the Na_2SO_3 reacted with the aldehyde [38] and affected the calculation of reaction conversion rate, sodium ascorbate was selected as the reducing agent in rapid sampling.

Typically, for the continuous micro-reaction system, the flow rates of crotonaldehyde solution (0.6 M), sodium chlorite solution (0.6 M) and hydrogen peroxide solution containing phosphate buffer salts (0.2 M H_2O_2 + 0.06 M H_3PO_4 + 0.11 M NaH_2PO_4) were 4.0 ml/min, 5.6 ml/min and 14.4 ml/min, respectively. Correspondingly, the molar ratio of crotonaldehyde, sodium chlorite, hydrogen peroxide, phosphoric acid and sodium dihydrogen phosphate was 1:1.4:1.2:0.35:0.65.

Batch reaction process

The procedure of the batch reaction was referred to Montanari's method [25].A solution of 0.95 g (8.4 mmol) of 80% $NaClO_2$ in 14 ml of water was added dropwise in 15 min to a stirred mixture of 0.42 g (6 mmol) of crotonaldehyde in 10 ml of acetonitrile and 0.47 g (3.9 mmol) of NaH_2PO_4 in 18 ml of water and 1.36 g (12 mmol) of 30% H_2O_2, keeping the temperature at 25 °C with water cooling. After the reaction was completed, the post-treatment steps were consistent with the continuous process.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s41981-024-00324-1.

Acknowledgements The authors gratefully acknowledge the support of the National Natural Science Foundation of China (22108264, 22378376) for this work.

Data availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest On behalf of all authors, the corresponding authors state that there is no conflict of interest.

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