Gas phase catalytic partial oxidation of toluene in a microchannel reactor

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Abstract

Gas phase partial oxidation of toluene over V/Ti oxide catalysts has been successfully performed in a microchannel reactor, which provides very good mass and heat transfer conditions. With the elimination of hot spots, which are known as the most negative factors for partial oxidation of hydrocarbons, steady and uniform reaction conditions can be achieved in the catalyst bed by using the microreactor. Since the best performance of the catalysts might be exploited, the selectivity of partial oxidation products of toluene has remarkably increased compared to the traditional packed fixed-bed reactor, even without the bother of modifying the catalysts, diluting the reactants or catalysts with inert contents to avoid hot spots or improve the diffusion and mixing. Furthermore, in virtue of its inherent safety features, when using pure oxygen as oxidant, the reactions were handled safely within the explosion limits in the microreactor. With TiO\textsubscript{2} carried V\textsubscript{2}O\textsubscript{5} as catalysts, the total selectivity of benzaldehyde and benzoic acid reaches around 60\%, and the toluene conversion is about 10\%. The conversion can go up without violent decline of selectivity, unlike most fixed bed reactors. Space time yield of 3.12 kg h\textsuperscript{-1} L\textsuperscript{-1} calculated on the basis of the channel volume has been achieved. The influence of operating conditions has been investigated in detail in the microreactor.

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1. Introduction

Microchannel reactors usually refer to miniaturized reaction systems fabricated by methods of microtechnology and precision engineering. The characteristic dimensions of the internal structures range from sub-micrometers to sub-millimeters [1,2]. When applied in chemical reactions, microreactors possess many fundamental advantages and accordingly exhibit great benefits that can not be achieved in traditional reactors, such as decreased physical sizes, increased surface-to-volume ratios, excellent mass and heat transfer capabilities, process safety, and therefore high yields, facility for scaling up and producing on site, etc. Due to their high specific surface areas and good mass and heat transfer capability and so on, microreactors have been widely applied in the field of heterogeneous catalytic reactions, including catalytic hydrogenations/dehydrogenations [3], ammonia oxidation [4], hydrogen combustion [5], fuel reforming [6–8] and selective oxidation of hydrocarbons [9–12], etc.

Selective oxidation is a very important class of reactions in the fine chemicals and petrochemical industries. It is a challenge to conquer the negative influence of side reactions on the yields and the risk of thermal runaway or explosion that spurs the development of new engineering concepts for this kind of reactions. Toluene selective oxidation is just such a reaction. The products of the reaction, both benzoic acid (BAc) and benzaldehyde (BA) are chemical intermediates of great importance to the chemical industry. At present, the main route of obtaining these compounds is the liquid phase oxidation of toluene, but there still exist unavoidable drawbacks in this process, such as undesired products formation, high cost on the successive separation operations and corrosion problems, etc. An alternative way is the gas phase oxidation of toluene. However, due to the total combustion and its strongly
exothermic and rapid reaction characteristic, the yields of the partial oxidation products are unsatisfactory and also the process is difficult to control and scale up.

Gas phase toluene oxidation is a complex reaction network composed of numerous parallel and consecutive reactions [13], and a simplified network was proposed [14] (Fig. 1). It is a strongly exothermic process (the reaction enthalpy of benzoic acid and total oxidation are −568.1 and −3772 kJ/mol, respectively), and the formation of hot spots is a serious problem due to the difficulty in fast heat removal. Like all other hydrocarbon’s oxidation, thermodynamics favors the formation of CO2 and water. Therefore, to obtain the intermediates BA and BAc, the reaction must be performed under a suitable condition. Existing literatures about the reaction mostly focus on catalysts and their modifications. The most detailed discussions are about V/Ti oxide catalysts [15,16] and it is generally accepted that the supported vanadia species are active components of partial oxidation and anatase TiO2 is the best support [17,18]. Some researches have been made on the modification of the V/Ti catalysts [19–22], the optimization of operating conditions [23–25], and the development of new reactors or catalysts different from the conventional packed bed reactors [26,27], but few exciting results are persuasive enough for industrialization. The highest BAc selectivity up to 80% with toluene conversion exceeding 70% was reported by Miki et al. [21], but plenty of water was induced and Liu et al. [25] also obtained fairly good BA and BAc selectivity under toluene conversion exceeding 70% with microwave heating. To lead the process to a more satisfactory performance for the purpose of industrialization, more efficient, more convenient and more economical ways need to be explored.

While performing oxidation reactions in microreactors, due to rapid heat transfer, the heat released can be removed rapidly and the formation of hot spots leading to the deep oxidation of the products can be avoided. On the other hand, good mass transfer means sufficient mix of the reactants and easy desorption of the partial oxidation products from the catalyst surfaces, so that more preferable product distribution may be attained. Furthermore, dimensions less than the quench distance for explosions result in a safer performance, and consequently the reactions can be handled safely in the explosion limits. So, the conversion and utilization ratio of the materials can be enhanced, the reactor can be more compact, and the separating task will be lightened greatly. The time and space yields of partial oxidation are expected to increase distinctly by using microreactor systems.

This research work aimed at employing a microchannel reactor to take on the toluene partial oxidation reaction, expecting increasing the selectivity and yields of the desired products to a pretty high degree. With the catalysts exerting their best capability, the new techniques should fulfill the primary demand of the industrialization such as selectivity and yields. We try to prove the feasibility of microchannel reactors for catalytic gas phase partial oxidation reactions, as one of a category of rapid and strongly exothermic reactions, and bring forward a new way for research and chemical synthesis.

2. Experimental

2.1. Catalyst preparation

Vanadium oxide carried on TiO2 (anatase) was employed in most reported literatures. The particle support was prepared by hydrolysis of Ti(SO4)2 with ammonia solution and keeping pH = 7. The obtained hydrosol was washed to eliminate SO4 and then dried in a refrigerant drier and calcined at 823 K for 3 h. After forming, crushing and sieving, particles with size of 30–50 mesh were impregnated with aqueous solution of NH4VO3 in appropriate amounts, followed by drying at 393 K and calcining at 773 K for 3 h. The amount of V2O5 loading was kept at 5% in weight. The surface area of the support was measured with nitrogen physisorption (self-made, DICP); the crystal structure was determined by XRD (Rigaku D/Max-rb, Japan). All the samples proved to be pure anatase with a specific surface area of 90 m2/g.

In the preliminary experiments, anatase prepared by sol–gel method and commercial TiO2 were also used as supports, and it was proved that those prepared by hydrolysis of titanic salt as above mentioned had moderate specific surface area and better behavior in reactions. Catalysts with different V2O5 loadings were made. Various additives such as K, Ag and Sb were separately or simultaneously added to the catalysts by consecutive impregnation of corresponding salt solutions. In the parallel experiments, the 5% V2O5/TiO2 catalysts were used.

2.2. Microreactor fabrication and configuration

A microchannel reactor was designed and fabricated to fulfill the requirement for carrying on a highly exothermic oxidation reaction. The channels were made in a stainless steel plate (75 mm × 75 mm) by micro-precision-machining. Fig. 2 shows the configuration of the plate. Both the width and depth of channels are 1 mm. Catalyst particles were packed within the 12 parallel channels. Quartz wool was set at each end of the catalysts to keep them from moving with the stream flow. A graphite sheet covered the plate to seal the channels. With an average deformation of 0.05 mm of the graphite compressed into the channels caused by press, the total volume of the channels was 0.342 mL. The catalyst amount and the flow

![Reaction network for the toluene oxidation (Ref. [14])](image-url)
mode can be adjusted by packing the catalyst in all or some of the channels and blocking some channels. Four grooves were made across in the back of the plate, where a thermal couple can be inserted and moved smoothly to measure the temperature of different region of the reaction plate.

The plate was firmly sandwiched between two stainless steel housings, which integrate four column heaters and a thermal couple besides inlet and outlet, as shown in Fig. 3. The heaters were inserted into both the top and bottom plates to keep the channels of the reaction plate maintain a certain temperature. The thermal couple for temperature control was inserted in the housing part beside the heaters. Stainless bolts were used to hold the different parts.

2.3. Experimental set-up and procedure

The studies were performed in the experimental set-up presented in Fig. 4. Toluene was injected with an isocratic pump (SSI series II, America), and oxygen (99.95%) was regulated through a mass flow controller (SevenStar D08-1D/ZM, Beijing, China). The feed was pre-mixed and preheated at 423 K in a pre-heater prior to entering the reactor. The lines connecting the pre-heater, the reactor and the collector were heated to avoid the condensation of the toluene and products. The reactions were carried out at atmospheric pressure under isothermal conditions, which were controlled by artificial intelligent temperature regulators (ÜGU AI, Amoy, China). A gas chromatograph (FULI 9790, Zhejiang, China) equipped with a TDX-01 packed column was used to analyze the gaseous products online. And the organic products were collected in 273 K acetone and successive 253 K salt-ice bath cold trap system, then separated by a capillary column (OV-101) and analyzed by FID in the same gas chromatograph. The data collections began after the reactions had come into steady conditions and under each certain condition the reaction continued for more than 2 h, during which the temperature detection and online gaseous products analysis provided proves that the system worked without fluctuation.

In order to obtain the preliminary information and for comparison, the reaction was also carried out in a fixed bed reactor packed with granular catalysts. The reactor is made of a 12 mm i.d. quartz tube and is heated by an oven. The catalysts have the same composition and same granularity with those used in the microreactor.

The conversion and selectivity are calculated with the method proposed in literature [28]. Conversion is defined as the ratio of mole number of toluene converted and the toluene injected into the reactor. The product selectivity is calculated on the basis of converted toluene. Only BAc, BA, CO and CO₂ are taken into account, while other products, such as benzene, maleic anhydride, phthalic anhydride, etc. also found in the products in a much minor quantity, are out of consideration. A simplified network is proposed to explain the parallel-consecutive mechanism (Fig. 5).

3. Results and discussions

3.1. General

The most widely used supported vanadium catalysts for partial oxidation of hydrocarbons were chosen in this work.
Catalysts screening was carried out in the fixed bed reactor. The experimental results showed that there was no obvious change in the catalytic activity by adding K, Ag or Sb to the catalysts or by varying the loading of V$_2$O$_5$ from 2 to 10 wt.%. However, increasing the surface area of the carrier brings an enhancement of activity. With the specific surface area of the TiO$_2$ changing from 20 to 70 m$^2$/g, the activity of the catalyst increased almost 10 times, but no obvious improvement was observed when the specific surface area rose to 90 m$^2$/g or larger. So, TiO$_2$ with an appropriate surface area and moderate V$_2$O$_5$ loading was selected in this work.

How to supply the catalysts to a microreactor is a critical problem for the application of the new conception. Some microchannels are made of active materials [9,29], but this method limits the wider application with chemical reactions. Great efforts have been made to provide porous oxide coatings as carriers for metal catalysts. Several techniques have been described for coating the inner surface of microchannel reactors with porous oxides, such as anode oxidation [10,30], vapor deposition [31], nanoparticle immobilization [32] and sol–gel technique [33], etc. Another more convenient type of solutions is to pack the catalyst powders or small pellets into the channels directly [34]. In this way, different reactions can be performed in a microreactor, in which different catalysts without special treatment can be easily packed and replaced. In this work, in order to avoid the drawbacks of this method, for instance, increase in pressure drop, risk of block, and loss of catalysts with the flow, particles of the same size with those used in the fixed bed reactor were employed. So, the performance of the microreactor can be directly compared with that of the fixed bed reactor and the effective heat transfer and removal capability possessed by the microreactor was emphasized. According to our preliminary experiments in the fixed bed reactor, there will be no internal mass diffusion effects with the catalyst particle size of 30–50 mesh. Catalysts with smaller particle size (80–120 mesh) were tried in the microreactor, but no obvious improvement of reaction performance was found in that case and channel blocking occurred in some parts, since there were some heavy coupling products and sometimes coke formed in the products. The design (see Section 2.2 and Figs. 2 and 3) gets rid of the hindrance of widespread use to a considerable degree. Anyway, almost all the heterogeneous reactions can be tried in the reactor with proper catalysts packed in the microchannels, and the quantity of the catalysts can be altered according to the demands.

For highly exothermic oxidations such as the toluene oxidation, the catalysts are always diluted with a certain ratio by inert particles to avoid the hot spot in the catalyst beds [21]. It is also testified by our experiments in the fixed bed, that higher dilution ratio leads to better selectivity, especially for BAc. However, even the dilution ratio is up to 10 by weight, still large temperature gradient exists. In the microreactor, catalysts without dilution are used to indicate its great capability of heat transfer and the advantages of this technique in improving the reaction conditions when used in partial oxidation reactions. Large amount of inert gas [27] or steam [21,24] has the same effect in assuring isothermal conditions along the reaction zone and lowering the hot spots temperature. In the experiments with the particle packed fixed bed reactor, nitrogen of higher ratio than in air and steam of certain quantity were added to the reactants to examine their function. Nitrogen has a slight positive effect on improving the selectivity of the partial oxidation products, but addition of water leads to an obvious increase of benzene along with its negligible benefit for the expected products. It might be caused by the alteration of the surface properties of the catalysts. However, a heavy price will be paid for the advantages brought by addition of inert mass, namely, great energy waste, loss of materials caused by exhaust, difficulty in products separation and collection, and lower productivity with higher reactor volume, etc. As oxidant, pure oxygen is a much better choice in that it leads to effective process intensification when enough selectivity and safety can be guaranteed.

The temperature has been well controlled in the microreactor. Even with the space velocity up to over 40,000 h$^{-1}$ and toluene conversion rate over 30 mol m$^{-3}$ s$^{-1}$ (both of the value are several times higher than those can be obtained in the fixed bed reactor), no detectable temperature fluctuating was found. In all cases, whenever a certain temperature is fixed, it varies just within 2 K at different time of the reaction or at different parts of the reactor. While in the fixed bed reactor, only with low concentration of toluene and oxygen can a relatively small temperature gradient be attained. It is apt to be out of control, resulting in temperature run-away and poor selectivity or even catalyst deactivation caused by overheating. In our experiments, the efforts of eliminating the mass transfer limitation didn’t provide any improvement to the reaction behavior. When monolith catalyst and wall-coated microreactor, which both do well in improving mass transfer, were used to carry out the reaction, relatively high activity but rather poor partial oxidation product selectivity was obtained. So, to get good reaction performance, heat removal is the most critical problem. And the microreactor used here does well in the aspect. With the high surface-to-volume ratio and the good heat conductivity of the metal materials, efficient heat removal can be realized and this kind of highly exothermic and bad tempered reaction can be easily handled in the microreactor. The flow rate, concentration and the composition of the reactants can be altered and regulated in a rather wide range according to the demands of the reaction itself. All of those are favorable factors for enhancing the selectivity in a partial oxidation reaction as confirmed in our experiments. Fig. 6
and heat transfer limitations are well eliminated and the catalyst can be used more efficiently.

It is generally accepted that for the toluene oxidation, the Mars and Van Krevelen model [35] is successful to describe the reaction. According to the model the reaction composes of two steps: the oxidation of toluene by the oxidized catalyst and the reoxidation of reduced catalyst, and the oxidation rate of toluene can be expressed as:

$$ R_T = \frac{1}{k_1 p_T} + \frac{\beta}{k_2 p_{O_2}} $$

in which $k_1$ and $k_2$ are rate constants for toluene oxidation and catalyst reoxidation reactions, respectively, $p_T$ and $p_{O_2}$ are the partial pressures of toluene and oxygen, and $\beta$ is the number of moles of oxygen consumed by oxidation of 1 mole toluene. After integration, rearrangement and application of $d p_{O_2} = \beta \, d p_T$, the equation also can be expressed as:

$$ - \frac{1}{S_v \ln(1 - X_T)} = \frac{1}{k_1} + \frac{1}{k_2} \ln(1 - X_{O_2}) $$

in which $S_v$ is the space velocity, $X_T$ and $X_{O_2}$ are the conversions of toluene and oxygen. The data got from the experiments, in which the reaction temperature and space velocity were fixed at 638 K and 31,000 h$^{-1}$ but partial pressures of toluene and oxygen varied, are presented in Fig. 7. The points fit the straight line well leads to the conclusion that the mechanism of the toluene oxidation can be explained by the redox theory proposed by Mars and Van Krevelen and the experimental data got in the microreactor can reveal the inherent characteristics of the catalytic reaction process well. From the straight line in Fig. 7 it can be seen that the rate constants $k_1$ and $k_2$ are in the same magnitude. So, the oxidation of toluene on the catalyst and the reoxidation of the catalyst are of the comparably important to the overall reaction of toluene oxidation.

![Image](image_url)
In general, for heterogeneous catalytic gas phase partial oxidation reactions, microreactor is a promising alternative to current traditional processes in improving selectivity and yield. Furthermore, with the elimination of the mass and heat transfer limitations, the true aspects of the reaction’s intrinsic characteristics might be well investigated in the microreactor. In the following sections, the results in the microreactor will be discussed in detail.

### 3.2. Effect of space velocity

The influence of gas hourly space velocity (GHSV), namely residence time is shown in Fig. 8. The results show that the toluene conversion decreases with the enhancement of space velocity and the trend is much more obvious at lower space velocity. This can be explained by that shorter residence time leads to the depression of the reactions occurring on the catalyst surface (steps 1, 3 and 4 in Fig. 5), especially the further oxidation of the products (step 4). This supposition is supported by the simultaneous increase in the total selectivity of partial oxidation products. In the middle part of the curves, with higher space velocity, deep oxidation of BAc to CO$_x$ is depressed, and simultaneously BAc coming from further oxidation of BA reduces. Consequently, the selectivity of BAc almost kept constant and the selectivity of BA and the total selectivity increased nearly linearly. The fact implies the presence of consecutive reactions of these products (see Fig. 5). At quite high space velocities (over about 36,000 h$^{-1}$), the selectivity especially BA selectivity drops but the toluene conversion doesn’t change much. It seems that too short residence time isn’t propitious to the formation of BA via route 1. However the reaction through route 2, which is likely to be a very high reaction rate, isn’t affected by the decrease of residence time and displays gradually to be dominant. At very low space velocities (less than 7700 h$^{-1}$), deep oxidation and formation of heavy coupling products and coke lead to much lower selectivity of partial oxidation products. So, to gain preferable conversion and selectivity, the space velocities should be selected between 8000 and 36,000 h$^{-1}$ according to the practical requirement. The microreactor exhibited remarkable production flexibility and capabilities here.

### 3.3. Effect of molar ratio of O$_2$ to toluene

In Fig. 9, toluene conversions and product selectivities are plotted as a function of the molar ratio of O$_2$ to toluene in the feed. Toluene conversion increases smoothly and selectivities of both BAc and BA decrease slightly when the molar ratio of O$_2$ to toluene increases from 2 up to about 7. At small molar fractions of O$_2$ (O$_2$/toluene $< 2$), more O$_2$ speeds up the consecutive reaction of BA to BAc, so the selectivity of BAc increases apparently and the selectivity of BA decreases. As a result, the total selectivity reaches the maximum and keeps constant with the increase of the O$_2$ fraction. When out of this range, especially molar ratio of O$_2$ to toluene higher than 8, it leads to deep oxidation of BAc to CO$_x$, so the BAc selectivity goes down rapidly. It is clear that higher toluene conversions are achieved at larger O$_2$ fraction, indicating that the reaction rate increases with the enhancement of the O$_2$ concentration in the feed. When O$_2$ is excessive, the conversion increases rapidly with a similar rapid drop in the selectivity. Direct oxidation might be greatly enhanced and lead to a sharp rise of toluene conversion and poor partial oxidation selectivity with most toluene oxidized to CO$_x$. The transition happens at O$_2$/toluene $\approx 6.5$, a number between 5.5 and 9, also the stoichiometric ratio of O$_2$ when toluene is completely oxidized to CO or CO$_2$.

### 3.4. Effect of reaction temperature

As a complex reaction network with several consecutive and parallel reactions, the toluene oxidation is very sensitive to temperature. The influence of reaction temperatures on the reaction activity is shown in Fig. 10. The toluene conversion increases with the reaction temperature. This is supposed to be caused by the speeding up of the consecutive oxidation of BAc to CO$_x$ (step 4 in Fig. 5). Around 640 K, the toluene conversion
begins to go up linearly with a much greater speed; from 643 to 683 K, it changes from 14.54 to 69.89%, meanwhile, the BAc selectivity increases dramatically. At low temperatures (<620 K), the selectivity of BA drops constantly and the selectivity of BAc passes through a maximum while the total selectivity does not change much with the temperature, which points out a parallel route of the formation of BA and COx (routes 1 and 2 in Fig. 5). The formation of BAc seems strongly affected by the reaction temperature with a complicated process. To get a preferable product distribution, there exists an optimal temperature region. More studies should be done on the reaction kinetics for an in-depth understanding of its mechanism.

4. Conclusions

The present study of the gas phase catalytic partial oxidation of toluene in the microchannel reactor reveals the potential of applying the microreaction technology in the chemical synthesis field. For this kind of high temperature and strongly exothermal reaction, the microreactor shows distinct advantages over traditional fixed bed reactors. Efficient mass and heat transfer in the microreactor assures that the reaction can be performed in a well-controlled manner, and that higher selectivity and higher purity of the products can be achieved.

With V/Ti oxide as catalysts and pure oxygen as oxidant, remarkable improvement of partial oxidation product selectivity can be obtained in the microreactor, at least twice of those in the fixed bed reactor under preferable toluene conversions. The throughput of BAc and BA reaches 3.12 kg h⁻¹ L⁻¹, calculated on the basis of the channel volume. Also rather high production flexibility is available, since the operating conditions can be easily altered and maintained steady in a very wide range, if not mentioned numbering-up approach. The reaction was easily handled and controlled under various conditions favorable to the process, for instant, at a high temperature, a high space velocity and high reactant concentrations, and even in the explosion regime, etc. With no mass and heat transfer limitations, the true reaction characteristics can be understood better through the experiments in the microchannel reactor.

Space velocity, feed composition and reaction temperature are crucial factors affecting the reaction performance. Toluene oxidation is a very complex reaction networks and to gain better results, all the possible factors need to be taken into consideration. Further efforts are necessary on the process to search for the actual mechanism, new and more favorable operating conditions, and better catalysts. The concept of utilizing microreactors in this study has provided a hopeful access for addressing the aforementioned issues.

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