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Continuous phenol hydroxylation over ultrafine TS-1 in a side-stream ceramic membrane reactor

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Abstract−A side-stream ceramic membrane reactor system was developed that can facilitate the in situ separation of ultrafine catalysts from the reaction mixture and make the production process continuous. Continuous hydroxylation of phenol to dihydroxybenzene over ultrafine titanium silicalites-1 (TS-1) was taken as a model reaction to evaluate the feasibility and performance of the membrane reactor system. The effects of membrane pore size and operation conditions (residence time, temperature, catalyst concentration, phenol/H_2O_2 molar ratio) on the performance of the reactor system were examined via single factor experiments. We demonstrated that the membrane pore size and operation conditions greatly affect the conversion, selectivity and filtration resistance. The phenol conversion and dihydroxybenzene selectivity remain stable at about 11% and 95% in a 20-h continuous run, respectively.

Key words: TS-1, Phenol Hydroxylation, Membrane Reactor, Ceramic Membrane, Stability

INTRODUCTION

Ultrafine catalysts have found a considerable number of applications in many fields such as organic synthesis, environmental protection and photocatalysis due to their special structures [1-3]. They can be applied in the form of powder suspended in slurry or immobilized on various supporting media. In fact, catalysts in suspension have a better efficiency than immobilized ones [4]. However, in that case, how to effectively recover the ultrafine catalysts from the slurry is a key issue from the point of view of practical application. One of the most promising methods to solve this problem is to couple the heterogeneous catalytic reaction with the membrane separation to structure a membrane reactor, in which the membrane facilitates the in situ separation of ultrafine catalysts from the reaction mixture [5].

Recent advancement in membrane technology, especially in microand ultra-filtration, has given an impetus to the development of membrane reactors. Generally, membrane reactors for heterogeneous catalysis can be divided into two configurations: submerged (immersed or integrated) type, which combines reaction and separation zone in a single unit of equipment; and side-stream (recirculated or external) type, where the reaction takes place in a stirred reaction vessel and the separation of the catalysts occurs in a separate crossflow membrane filtration unit [6]. Although submerged membrane reactors have received more attention owing to lower energy consumption and less occupied area [7-9], most researches have been restricted to laboratory study rather than industrial applications. For a submerged membrane reactor, the membrane modules are submerged in the reactor, so it is difficult to clean and replace the membrane modules. Furthermore, the filtration area is limited, resulting in a limited productivity. These characteristics will limit the process industrialization. Side-stream membrane reactors have greater advantages over submerged ones in industrial applications. On one hand, the separated membrane modules are easier to be clean and replace. On the other hand, the side-stream membrane reactors are more flexible and easier to operate, control and scale-up due to the segregation of reaction zone and separation zone [10,11]. At present, most of the studies, basically using polymeric membranes, are mainly focused on the biochemical process and wastewater treatment [12-15]. There are few investigations based on the chemical or petrochemical production processes, using inorganic membranes as the separation unit [16].

In this work, we have constructed a side-stream ceramic membrane reactor system and taken the hydroxylation of phenol to dihydroxybenzene over ultrafine titanium silicalites-1 (TS-1) as a model reaction to investigate the continuous process of combining the heterogeneous catalytic reaction with the membrane separation. Dihydroxybenzene (DHB), including catechol (CA) and hydroquinone (HQ), are important chemical intermediates, which are widely used as photographic chemicals, antioxidants, and polymerization inhibitors [17]. Resulting from its advantages such as being environmentally benign and having a high atom economy, phenol hydroxylation catalyzed by ultrafine TS-1 catalysts with H_2O_2 as the oxidant is a promising process for DHB production [18]. In our previous work [19], a submerged membrane reactor was developed for the phenol hydroxylation over TS-1, and the effects of operation conditions on the performance of the submerged membrane reactor were investigated in detail. To obtain more useful references for the industrialization of phenol hydroxylation over TS-1, we developed a side-stream membrane reactor for the reaction system based on the advantages of side-stream membrane reactor as presented above. In

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this study, the most attention was given to investigate the effects of membrane pore size and operation conditions on the properties of phenol hydroxylation and membrane filtration.

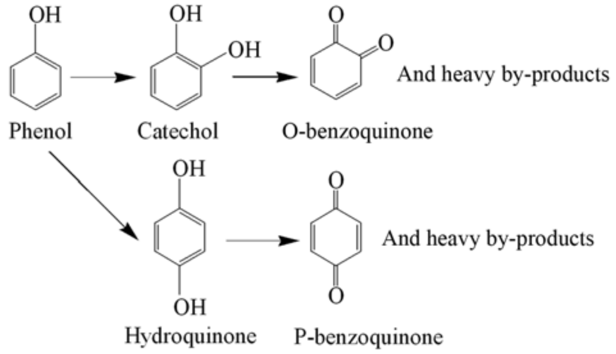
EXPERIMENTAL

1. Materials

TS-1 catalyst (average particle size, 260 nm; specific surface area, 486 $m^2 \cdot g^{-1}$; Si/Ti molar ratio, 33) was provided by Lianyungang Sanjili Chemical Industry Co., Ltd., China. Phenol was supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd., China. HQ, CA, 30% H_2O_2 and sodium hydroxide were all obtained from Sinopharm Chemical Reagent Co., Ltd., China. Methanol (>99.9% chromatography grade) was provided by Yuwang Group and pure water by Hangzhou Wahaha Group. Deionized water (electrical conductivity <12 $\mu s \cdot cm^{-1}$) was homemade. All materials were of analytical grade and used without further treatment.

2. Continuous Ceramic Membrane Reactor System

A side-stream ceramic membrane reactor system, as shown in Fig. 1(a), was designed and constructed on a laboratory scale. The system mainly consisted of a slurry tank, a centrifugal pump, a cross-flow ceramic membrane module, a feeding system, a products-collecting system and a heating system. A stainless slurry tank with a working volume of 4 L was equipped with an external jacket for temperature controlling. A centrifugal pump (Grundfos, Denmark) was used to pump the feed suspension through the membrane module. The schematic diagram of the ceramic membrane module is presented in Fig. 1(b). The module mainly consisted of three parts bolted together. During the reaction, the reaction solution flowed through the membrane and partly permeated out under the pressure. The used single tubular ceramic membranes and ceramic support were provided by Jiusi High-Tech Co., Ltd., Nanjing, China. The outer diameter, inner diameter and filtration area were 12 mm, 8 mm and 45 cm^2, respectively. The ceramic membrane is made up of a fine layer of ZrO_2 (normal pore size of 50 or 200 nm) coated on the inner wall of a tubular α-Al_2O_3 support. The tubular α-Al_2O_3 support has a normal pore size of 2,000 nm. Two peristaltic pumps (Baoding Longer Precision Pump Co., Ltd., China) were used to feed phenol and H_2O_2 aqueous solution, respectively. The products were collected in a graduated cylinder.



Scheme 1. Phenol hydroxylation with H_2O_2 over TS-1 catalyst.

3. Phenol Hydroxylation Experiments

According to the GC-MS results of reaction products (data not shown here), the phenol hydroxylation with H_2O_2 over TS-1 catalyst can be simply described as Scheme 1, in agreement with a previous report [20]. Catechol and hydroquinone, as the target products, may be further oxidized to unexpected by-products such as o-benzoquinone, p-benzoquinone and other heavy by-products.

We divided the experimental procedure of phenol hydroxylation reaction into two stages, as in our previous work [19]. The first stage was a batch reaction process. After adding given amounts of phenol solution and TS-1 catalyst, we sealed the reactor and turned on the centrifugal pump, and then the reaction system was heated by circulating hot water. When the temperature reached the setting value, 30% H_2O_2 solution was feed into the reactor and the reaction started. After desired amounts of H_2O_2, were fed in, the feeding was stopped and the reaction was run for another 2 h. The second stage was a

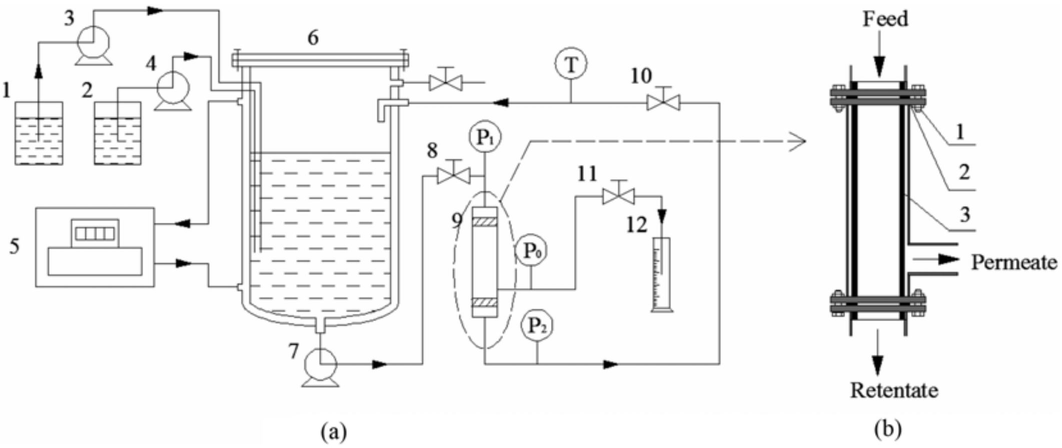


Fig. 1. Schematic diagram of the side-stream ceramic membrane reactor system (a) and the ceramic membrane module (b).

(a) 1. Reserve tank of phenol solution
2. Reserve tank of hydrogen peroxide solution
3. Phenol solution feed pump
4. Hydrogen peroxide solution feed pump
5. Thermostatic water bath
6. Reactor
7. Centrifugal pump
8, 10, 11, 13. Valves
9. Ceramic membrane module
12. Product collector

(b) 1. Bolt and nut
2. Sealing washer
3. Ceramic membrane

Table 1. Experimental variables for the phenol hydroxylation reaction

Membrane pore size/nm	Residence time/h	Reaction temperature/°C	Catalyst concentration/kg·m^3	Phenol/H_2O_2 molar ratio
50	4.8	60	4.7	3
200	6.0	70	7.0	5
2000	8.0	80	14.1	7
	9.6	90	20.1	9

continuous reaction process. The phenol solution and 30% H_2O_2 solution were fed into the reactor at the same phenol/H_2O_2 molar ratio with the batch process, and the products were taken out simultaneously in the permeate side at a certain flow rate by controlling the valve 11 as shown in Fig. 1(a), equaling the total feeding flow rate. Thus, the liquid level in the reactor remained constant and the system was operated in a constant membrane flux. The suspended TS-1 catalysts were retained in the reactor by the ceramic membrane. With respect to the investigations of membrane pore size and operation conditions, the continuous reaction process was conducted for 4 h. The experimental variables investigated in the present work are given in Table 1.

After each run, the system was emptied and thoroughly rinsed with tap water to remove residual reaction mixture, cleaned by circulating 1 wt% NaOH solution at 80 °C and 1 wt% HNO_3 solution at 50 °C for several hours with the permeate line open, and rinsed with deionized water until the pH returned to about 7. Only if the pure water flux of the used membrane was greater than 95% that of the fresh, the membrane was regarded as clean and used for the next run.

The products were collected from the outlet of the reactor at set intervals and analyzed by an HPLC system (Agilent 1200 Series, USA) equipped with a diode array detector (DAD) and an autosampler. 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 40% methanol and 60% water at a flow rate of 1 ml·min^{-1} was used. External standard method was employed for determining the concentrations of phenol and DHB. Phenol conversion and DHB selectivity were calculated on the basis of the initial phenol concentration, according to Eqs. (1) and (2), respectively:

$$X=\frac{C_{phenol(o)}-C_{phenol(p)}}{C_{phenol(o)}} \tag{1}$$

$$S=\frac{C_{CA}+C_{HQ}}{C_{phenol(o)}-C_{phenol(p)}} \tag{2}$$

where X is the phenol conversion, S is the DHB selectivity, $C_{phenol(o)}$ is the initial phenol concentration in the feed (mol·L^{-1}), $C_{phenol(p)}$ is the phenol concentration in the outlet of the reactor (mol·L^{-1}), C_{CA} and C_{HQ} are the concentration of CA and HQ in the outlet of the reactor (mol·L^{-1}).

The inevitable membrane fouling can degrade the membrane performance and reduce service life, which makes more frequent membrane cleaning and replacement necessary and then increases operating costs. Because the coupling process was operated at a constant membrane flux, the transmembrane pressure would increase with operation time due to the membrane fouling. Therefore, the membrane fouling can be monitored by the change of the transmembrane pressure. According to Darcy's law [21], the filtration resistance was obtained from the transmembrane pressure and the membrane flux:

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

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

To estimate the retention of the TS-1 catalyst by the membrane, the concentrations of silicon and titanium elements in the permeate were analyzed by inductively coupled plasma emission spectroscopy (ICP, Optima 7000DV, USA).

4. Membrane Characterization

Morphology of membrane surface and cross section were visually examined using a field emission scanning electron microscope (FESEM, S-4800 II, Hitachi). The membranes were gold-coated before scanning.

RESULTS AND DISCUSSION

The side-stream membrane reactor is a combination of a chemical reaction with a membrane separation process, in which some important factors affecting the catalytic performance also affect the separation efficiency. Therefore, the effects of membrane pore size and operation conditions including residence time, reaction temperature, catalyst concentration and phenol/H_2O_2 molar ratio on the phenol conversion and DHB selectivity were investigated by using single factor experiments, and meanwhile the corresponding filtration resistances were also evaluated.

1. Effect of Membrane Pore Size

The membrane pore size is a key factor for the membrane reactor system because it determines the catalyst retention ratio and the membrane flux, and therefore affects the performances of the coupling system. Fig. 2 illustrates the effect of membrane pore size on the phenol conversion, DHB selectivity, filtration resistance and catalyst retention ratio. When a tubular α-Al_2O_3 support with a pore size of 2,000 nm was used as the separation unit, after 2-h run, the discharge flow rate (i.e., the membrane flux) could not reach the demand equaling to the feeding flow rate due to the severe membrane fouling as shown in Fig. 2(c), so in this case the phenol hydroxylation experiment was only carried out for 2 h.

In the studied experimental range for the present reactor system, the membrane pore size has little effect on the conversion but great effect on the selectivity, filtration resistance and retention ratio. As can be seen from Fig. 2(b) and (c), the selectivity varies significantly with the membrane pore size and follows the order: 200 nm>50 nm> 2,000 nm, while the opposite trend is found for the filtration resistance. To obtain the same membrane flux, the needed transmembrane pressure for the membrane with a pore size of 50 nm will be

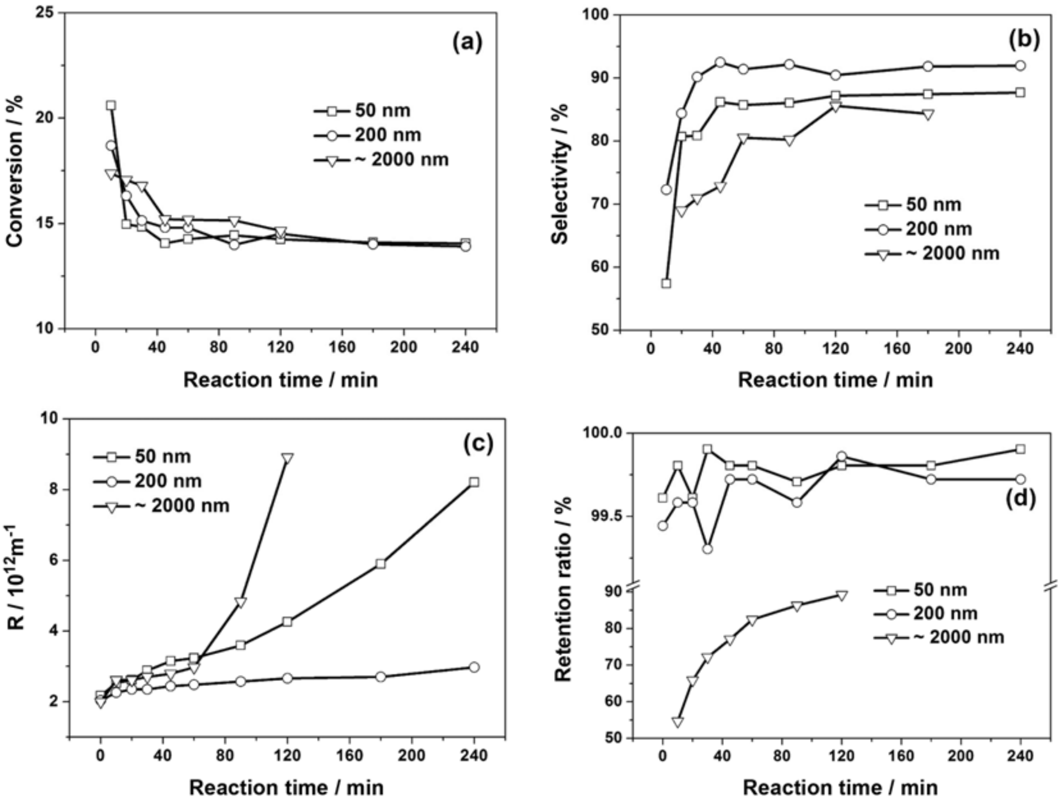


Fig. 2. Effect of membrane pore size on the conversion (a), selectivity (b), filtration resistance (c) and catalyst retention ratio (d) (C_{phenol}= 1.5 mol·L^{-1}, $C_{H_2O_2}$=0.3 mol·L^{-1}, reaction temperature is 80 °C, residence time is 8 h, catalyst concentration is 7 kg·m^{-3}).

larger than others because of the smaller pore size, which may make more TS-1 catalyst adsorb on the membrane surface. As a result, the effective catalyst concentration in the slurry tank will decrease. For the support, the pore size is much larger than the catalyst particle size, and some TS-1 catalyst particles can permeate through the support, resulting in a pore blocking and a decrease of effective catalyst concentration in the slurry tank. Pore blocking essentially results in a decrease of the membrane porosity [22], and the needed transmembrane pressure will be also larger to obtain the same membrane flux. As discussed below in Fig. 5, the catalyst concentration has no obvious effect on the conversion but significant effect on the selectivity, and a higher selectivity can be obtained at higher catalyst concentration. So the membrane pore size has little effect on the conversion, and the selectivity for the membrane with a pore size of 50 nm or the support is lower. According to Eq. (3), the filtration resistance is proportional to the transmembrane pressure, and so the filtration resistance for the membrane with a pore size of 50 nm or the support is higher. Compared to the membrane with a pore size of 50 nm, the effect of the permeating of TS-1 catalyst through the support on the selectivity and filtration resistance is greater for the support, leading to a lower selectivity and a higher filtration resistance. The increase of filtration resistance all along the reaction time as revealed in Fig. 2(c) should be due to the accumulation of by-products on the membrane surface [23].

From Fig. 2(d), the retention ratio of TS-1 catalyst remained at about 100% in a 4-h run when the membrane with a pore size of 200 or 50 nm was used, indicating the complete retention of TS-1 catalyst. For the support, the retention ratio of TS-1 catalyst is lower than 100% and increases from 54.6% to 89.3% in the 2-h run. As discussed above, the ultrafine TS-1 catalyst can permeate through the support, which will make the retention ratio lower. The adsorption of TS-1 catalyst in the support pore makes the pore size gradually decrease, leading to an increase of retention ratio with time.

In consideration of all the factors mentioned above, a ceramic membrane with a pore size of 200 nm was employed in subsequent experiments.

2. Effect of Residence Time

Residence time was calculated as a total volume of the reaction solution divided by the flow rate and could be considered as the average time that reactants spent inside the reactor. Here we kept the total reaction volume constant, so there is one-to-one correspondence between residence time and feed flow rate. The effect of residence time on the phenol hydroxylation is shown in Fig. 3. In the studied experimental range for the present reactor system, with increasing residence time, the conversion almost remains stable while the DHB selectivity increases until a maximum value is observed at the residence time of 8 h and then decreases. For the phenol hydroxylation, in order to obtain higher DHB selectivity, the phenol/H_2O_2 molar ratio is often higher [24,25]. During investigating the effect of residence time, the phenol/H_2O_2 molar ratio is controlled at 5, so the phenol is excessive compared to H_2O_2. According to the kinetics of phenol hydroxylation over TS-1 [10], the H_2O_2 in the reactor will be completely consumed in 2 h in the studied experimental range. So the phenol conversion will increase until a maximum value in 2 h and then stay stable. In the present work, the residence time is changed from 4.8 to 9.6 h, so the conversion almost remains stable.

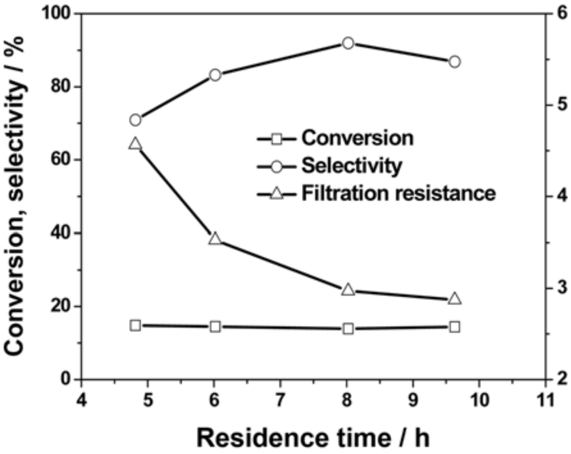


Fig. 3. Effect of residence time on the conversion, selectivity and filtration resistance (C_{phenol}=1.5 mol·L^{-1}, $C_{H_2O_2}$=0.3 mol·L^{-1}, membrane pore size is 200 nm, reaction temperature is 80 °C, catalyst concentration is 7 kg·m^{-3}).

The trend of DHB selectivity with residence time may be caused by two factors. On one hand, the feed flow rate needs to be decreased for increasing the residence time. The lower feed flow rate of H_2O_2 will lead to a lower H_2O_2 concentration in a certain time and a higher selectivity. On the other hand, the DHB selectivity will decrease with increasing residence time due to the further oxidation of DHB to benzoquinone or heavy by-products by the consecutive reactions according to the reaction scheme. It is seen from Fig. 3 that the filtration resistance decreases obviously with an increase of residence time. To increase residence time, the feed flow rate needs to be decreased. As a result, the membrane flux also has to be decreased to keep the liquid level constant. Thus the needed transmembrane pressure is reduced, resulting in the decrease of filter cake thickness and filtration resistance [26]. Considering the reaction selectivity and filtration resistance, the appropriate residence time is 8 h.

3. Effect of Temperature

Fig. 4 shows the effect of reaction temperature from 60 to 90 °C on the phenol hydroxylation. With increasing reaction temperature, there is no obvious change in the conversion of phenol in the studied experimental range for the present reactor system, like the effect of residence time as shown in Fig. 3. The DHB selectivity fluctuates in the experimental range and reaches its maximum at 80 °C, similar to our previous work [19]. The main reaction rate and the side reaction rate increase simultaneously with increasing temperature. The selectivity depends on the relation between the main and side reaction rates. When the main reaction is dominant, the selectivity will increase, and vice versa, leading to the fluctuant DHB selectivity. From Fig. 4, the filtration resistance increases gradually as the temperature increases. This is an unexpected phenomenon, because a higher temperature is anticipated to reduce the filtration resistance due to the decrease of fluid viscosity [19]. The possible reason for the unexpected result is as follows. Both molecular Brownian motion and catalyst particle movement can be aggravated at higher temperature. As a result, the opportunities for by-product molecules and catalyst particles to deposit on the membrane surface increase, resulting in a thicker filter cake and higher filtration resistance. Taking into account all these factors, the reaction temperature of 80 °C is considered to be appropriate.

4. Effect of Catalyst Concentration

The effect of catalyst concentration on the coupling process is examined and the results are illustrated in Fig. 5. In the studied experimental range for the present reactor system, with increasing catalyst concentration, the conversion almost remains stable, while the DHB selectivity first increases until 14.1 kg·m^{-3} and then decreases slightly. The decrease of DHB selectivity may be due to the aggravation of side reactions as mentioned in Scheme 1 when using excessive catalyst [27]. It is interesting that the filtration resistance shows an opposite trend compared to the change of DHB selectivity. The filtration resistance clearly depends on the filter cake thickness and the specific cake resistance. Obviously, there is a positive correlation between the filter cake thickness and the catalyst concentration. However, the filtration resistance decreases with increasing catalyst concentration from 4.7 to 14.1 kg·m^{-3} as shown in Fig. 5, which strongly proves the dominating factor of filtration resistance

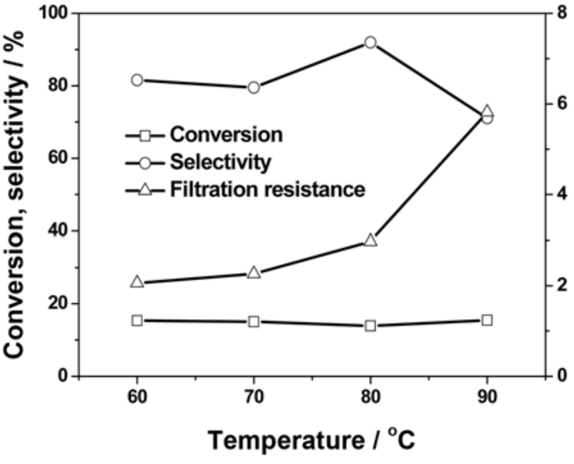


Fig. 4. Effect of reaction temperature on the conversion, selectivity and filtration resistance (C_{phenol}=1.5 mol·L^{-1}, $C_{H_2O_2}$=0.3 mol·L^{-1}, membrane pore size is 200 nm, residence time is 8 h, catalyst concentration is 7 kg·m^{-3}).

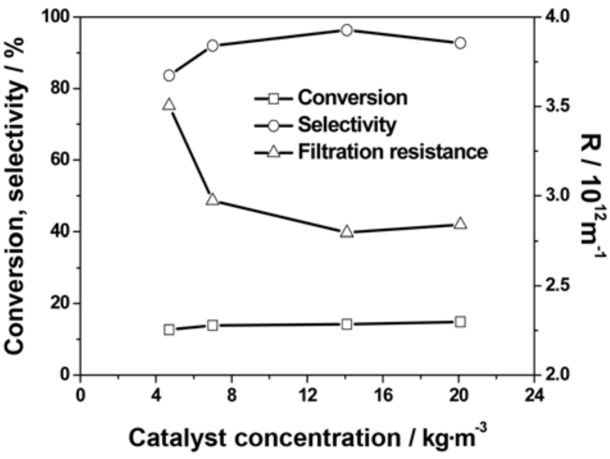


Fig. 5. Effect of catalyst concentration on the conversion, selectivity and filtration resistance (C_{phenol}=1.5 mol·L^{-1}, $C_{H_2O_2}$=0.3 mol·L^{-1}, membrane pore size is 200 nm, reaction temperature is 80 °C, residence time is 8 h).

in this study is the specific cake resistance rather than the filter cake thickness. Therefore, with respect to the studied reaction system, the membrane fouling is together caused by the catalyst cake and the by-products. For the case of high selectivity the cake layer that is mainly composed of catalyst particles is porous and the corresponding filtration resistance is lower, whereas for low selectivity a dense cake layer is formed on the membrane surface by the combination of particles and by-products, leading to a higher filtration resistance. Similar particle/colloid fouling was also found [23,28,29]. It has been reported that the organic matter has a great effect on the nature of cake layer, because it can be adsorbed onto the surfaces of particles in the cake layer and change the permeability of the cake layer [29]. The effect of by-products on the filtration resistance will be further studied in the future. According to the above results, an optimal catalyst concentration of 14.1 kg·m^{-3} is employed for further experiments.

5. Effect of Phenol/H_2O_2 Molar Ratio

Fig. 6 presents the effect of molar ratio of phenol/H_2O_2 in the feed on the coupling process. With increasing phenol/H_2O_2 molar ratio, the phenol conversion decreases while the DHB selectivity increases. With respect to the continuous phenol hydroxylation, the total feed (including the phenol and the H_2O_2) flow rate is kept at 6 mL·min^{-1}, therefore, when the feed flow rate of phenol increases, the feed flow rate of H_2O_2 must decrease, resulting in the increase of molar ratio of phenol/H_2O_2 in the feed. In this study, the phenol is excessive compared to H_2O_2, so the decrease of H_2O_2 makes some phenol not react and a lower conversion is obtained. Meanwhile, the formed dihydroxybenzene in the reactor is not easy to be oxidized to unexpected by-products due to the decrease of H_2O_2, leading to a higher DHB selectivity. As illustrated in Fig. 6, the filtration resistance decreases with increasing phenol/H_2O_2 molar ratio, which is opposite to the change of DHB selectivity. The phenomenon is similar to the results in Fig. 5, further indicating the key influence of by-products on the filtration resistance. Taking into account the conversion, selectivity and filtration resistance, the phenol/H_2O_2 molar ratio of 7 in the feed for the coupling process is chosen.

Accordingly, the feasible ceramic membrane pore size and operation conditions obtained via single factor experiments for the coupling process are as follows: membrane pore size 200 nm, residence time 8 h, temperature 80 °C, catalyst concentration 14.1 kg·m^{-3} and molar ratio of phenol/H_2O_2 7.

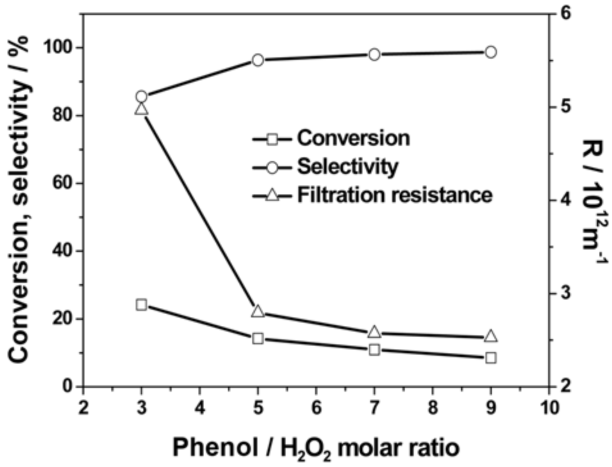


Fig. 6. Effect of the molar ratio of phenol/H_2O_2 on the conversion, selectivity and filtration resistance (membrane pore size is 200 nm, reaction temperature is 80 °C, residence time is 8 h, catalyst concentration is 14.1 kg·m^{-3}).

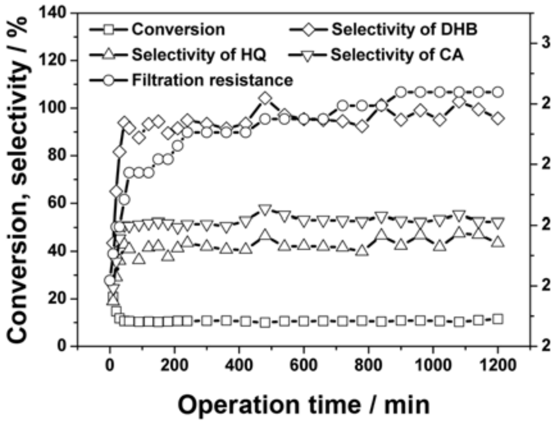


Fig. 7. Long-term operating stability of the continuous side-stream ceramic membrane reaction system (C_{phenol}=1.5 mol·L^{-1}, $C_{H_2O_2}$ =0.214 mol·L^{-1}, membrane pore size is 200 nm, reaction temperature is 80 °C, residence time is 8 h , catalyst concentration is 14.1 kg·m^{-3}).

6. Feasibility of the Continuous Reaction Process

To investigate the feasibility of the continuous hydroxylation of phenol to DHB in the side-stream ceramic membrane reactor system, the reaction process was run for 20 h under the optimal operation conditions as discussed above. The change of conversion, selectivity and filtration resistance with operation time is presented in Fig. 7. The conversion decreases during an initial 40 min and then levels off around 11%, while the DHB selectivity first increases and then remains at about 95% through the reaction. The molar ratio of CA/HQ keeps around 1.3 through the reaction, similar with our previous work [19]. The initial decrease of conversion is likely caused by the adsorption of TS-1 catalyst particles on the clean membrane surface [19,30]. Lu et al. [19] and Jiang et al. [30] have all reported that the phenol conversion decreased significantly at the beginning of the operation and then decreased slowly in a submerged membrane reactor and a dual-membrane reactor, respectively. The further decrease of phenol conversion was considered to be due to the TS-1 catalyst deactivation by fouling because of heavy by-products. The phenomenon is not observed in the present work, possible because of the fact that fewer by-products formed at higher phenol/H_2O_2 molar ratio inhibit the catalyst deactivation in this study. As can be seen in Fig. 7, the filtration resistance first clearly increases and then increases slowly. The adsorption of TS-1 catalyst particles on the clean membrane surface should be responsible for the increase of filtration resistance during the primary stage, and the further increase may be due to the accumulation of by-products in the cake layer on the membrane surface with prolonging the operation time.

Table 2 lists the typical results from this work and compares them with data from different reactors under their respective optimal operation conditions as found in the literature [19,24,30,31]. Note that higher selectivity can be obtained with comparable conversion in the side-stream membrane reactor compared to the fixed-bed reac-

Table 2. Comparison of phenol conversion and DHB selectivity in various reactors

Reactor	Catalyst	Phenol conversion/%	DHB selectivity/%	Ref.
Fixed-bed reactor	TS-1/diatomite	12.0	67.4	[24]
Packed bed catalytic microreactor	TS-1	47.8	98.5	[31]
Catalytic wall microreactor	TS-1	44.6	98.4	[31]
Submerged membrane reactor	TS-1	17.0	90.0	[19]
Dual-membrane reactor	TS-1	15.0	95.0	[30]
Side-stream membrane reactor	TS-1	10.6	95.3	This work

tor [24]. The phenol conversion and DHB selectivity in the side-stream membrane reactor are all lower than those from a packed bed catalytic microreactor or catalytic wall microreactor, possibly because of the special reactor design of the microreactor [31]. Compared to other membrane reactors reported in our previous works [19,30], the performance of phenol hydroxylation in the present work is comparable; furthermore, the side-stream membrane reactor is easier to operate, control and scale-up.

7. Membrane Stability

An important consideration is the life of the ceramic membrane used in the continuous phenol hydroxylation. The fresh and used membranes were characterized by field emission scanning electron microscopy. In Fig. 8, no obvious difference exists between the fresh membrane surface and the used membrane surface, and the top membrane layer still remains well intact with the support after continuous using. The results indicate that the porous ceramic membrane used in the experiments has excellent thermal stability and chemical stability. A longer term run for the investigation of the ceramic membrane life in the continuous side-stream membrane reactor system is in progress.

CONCLUSIONS

A side-stream ceramic membrane reactor system has been developed for the continuous phenol hydroxylation to CA and HQ over ultrafine TS-1 catalyst. The phenol conversion, DHB selectivity and filtration resistance all clearly depend on the membrane pore size and operation conditions. Optimal membrane pore size and operation conditions for the coupling process are obtained by single factor experiments. The side-stream ceramic membrane reactor system can maintain a steady production of CA and HQ over 20 h. Meanwhile, the used ceramic membrane has excellent thermal stability and chemical stability. The present work demonstrates that the developed side-stream ceramic membrane reactor system is feasible for

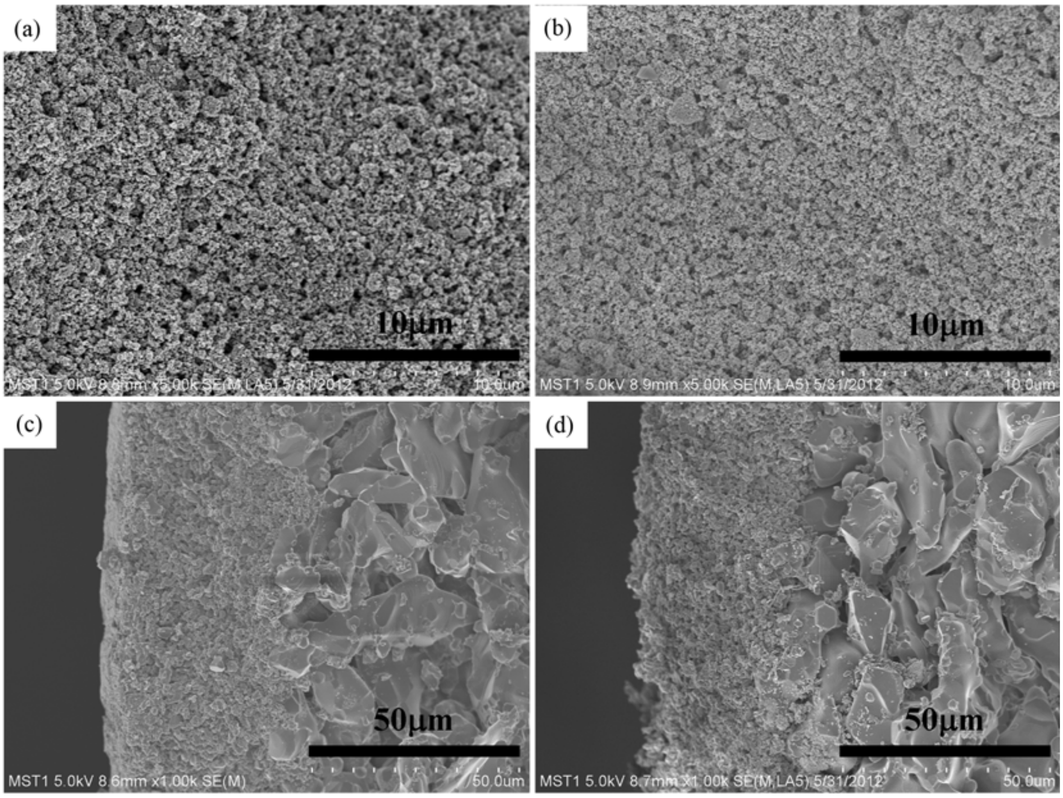


Fig. 8. FESEM pictures of porous ceramic membrane: (a) top view of fresh membrane; (b) top view of used membrane; (c) side view of fresh membrane; (d) side view of used membrane.

continuous heterogeneous catalytic reactions over ultrafine catalysts.

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REFERENCES

1. R. M. Mohamed, D. L. McKinney and W. M. Sigmund, *Mater. Sci. Eng. R*, **73**, 1 (2012).
2. Y. Du, H. L. Chen, R. Z. Chen and N. P. Xu, *Appl. Catal. A: Gen.*, **277**, 259 (2004).
3. P. T. Anastas, M. M. Kirchhoff and T. C. Williamson, *Appl. Catal. A: Gen.*, **221**, 3 (2001).
4. S. Parra, S. Elena Stanca, I. Guasaquillo and K. Ravindranathan Thampi, *Appl. Catal. B: Environ.*, **51**, 107 (2004).
5. R. Z. Chen, Z. Bu, Z. H. Li, Z. X. Zhong, W. Q. Jin and W. H. Xing, *Chem. Eng. J.*, **156**, 418 (2010).
6. P. Le-Clech, V. Chen and T. A. G. Fane, *J. Membr. Sci.*, **284**, 17 (2006).
7. J. K. Shim, I.-K. Yoo and Y. M. Lee, *Process Biochem.*, **38**, 279 (2002).
8. P. Schoeberl, M. Brik, M. Bertoni, R. Braun and W. Fuchs, *Sep. Purif. Technol.*, **44**, 61 (2005).
9. Y. Y. Zhang, C. He, V. K. Sharma, X. Z. Li, S. H. Tian and Y. Xiong, *Sep. Purif. Technol.*, **80**, 45 (2011).
10. R. Z. Chen, H. Jiang, W. Q. Jin and N. P. Xu, *Chin. J. Chem. Eng.*, **17**, 648 (2009).
11. C. Visvanathan, R. B. Aim and K. Parameshwaran, *Crit. Rev. Env. Sci. Tec.*, **30**, 1 (2000).
12. J. G. Liu and Z. F. Cui, *J. Membr. Sci.*, **302**, 180 (2007).
13. M. Ebrahimi, L. Placido, L. Engel, K. S. Ashaghi and P. Czermak, *Desalination*, **250**, 1105 (2010).
14. H. Dhaouadi and B. Marrot, *Chem. Eng. J.*, **145**, 225 (2008).
15. A. Hasanoğlu, J. Romero, B. Pérez and A. Plaza, *Chem. Eng. J.*, **160**, 530 (2010).
16. W. Yang, N. Cicek and J. Ilg, *J. Membr. Sci.*, **270**, 201 (2006).
17. J. Wang, J. N. Park, H. C. Jeong, K. S. Choi, X. Y. Wei, S. I. Hong and C. W. Lee, *Energy Fuels*, **18**, 470 (2004).
18. U. Wilkenhöner, G. Langhendries, F. van Laar, G. V. Baron, D. W. Gammon, P. A. Jacobs and E. van Steen, *J. Catal.*, **203**, 201 (2001).
19. C. J. Lu, R. Z. Chen, W. H. Xing, W. Q. Jin and N. P. Xu, *AIChE J.*, **54**, 1842 (2008).
20. H. Liu, G. Z. Lu, Y. L. Guo, Y. Guo and J. S. Wang, *Chem. Eng. J.*, **116**, 179 (2006).
21. W. X. Li, W. H. Xing and N. P. Xu, *Desalination*, **192**, 340 (2006).
22. A. Broeckmann, J. Busch, T. Wintgens and W. Marquardt, *Desalination*, **189**, 97 (2006).
23. R. Z. Chen, Y. Du, Q. Q. Wang, W. H. Xing, W. Q. Jin and N. P. Xu, *Ind. Eng. Chem. Res.*, **48**, 6600 (2009).
24. H. Liu, G. Z. Lu, Y. L. Guo, Y. Guo and J. S. Wang, *Chem. Eng. J.*, **108**, 187 (2005).
25. L. H. Callanan, R. M. Burton, J. Mullineux, J. M. M. Engelbrecht and U. Rau, *Chem. Eng. J.*, **180**, 255 (2012).
26. S. Mahesh Kumar, G. M. Madhu and S. Roy, *Sep. Purif. Technol.*, **57**, 25 (2007).
27. S. Li, G. L. Li, G. Y. Li, G. Wu and C. W. Hu, *Micropor. Mesopor. Mater.*, **143**, 22 (2011).
28. Z. X. Zhong, W. H. Xing, X. Liu, W. Q. Jin and N. P. Xu, *J. Membr. Sci.*, **301**, 67 (2007).
29. S.-A. Lee, K.-H. Choo, C.-H. Lee, H.-I. Lee, T. Hyeon, W. Choi and H.-H. Kwon, *Ind. Eng. Chem. Res.*, **40**, 1712 (2011).
30. H. Jiang, L. Meng, R. Z. Chen, W. Q. Jin, W. H. Xing and N. P. Xu, *Ind. Eng. Chem. Res.*, **50**, 10458 (2011).
31. K. Yube, M. Furuta and K. Mae, *Catal. Today*, **125**, 56 (2007).