

## Research Article

# Nanofiber-Membrane-Supported $\text{TiO}_2$ as a Catalyst for Oxidation of Benzene to Phenol

Chanbasha Basheer<sup>1,2</sup>

<sup>1</sup> Department of Chemistry, King Fahd University of Petroleum and Minerals, P.O. Box-1509, Dhahran 31261, Saudi Arabia

<sup>2</sup> Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

Correspondence should be addressed to Chanbasha Basheer; [cbasheer@kfupm.edu.sa](mailto:cbasheer@kfupm.edu.sa)

Received 13 May 2012; Revised 10 June 2012; Accepted 10 June 2012

Academic Editor: Veysel T. Yilmaz

Copyright © 2013 Chanbasha Basheer. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We applied a simple, low-cost design of glass capillary microreactor for the catalytic oxidation of benzene to phenol at ambient conditions. Polyvinylchloride-nanofiber-membrane-supported titania nanoparticle ( $\text{TiO}_2$ -PVC) as catalyst and in situ production of hydroxyl radicals as oxidant. The reaction was monitored by gas chromatography-mass spectrometry (GC-MS). The reaction conditions were optimized and the performance of the microreactor was then compared with the conventional laboratory scale reaction which used hydrogen peroxide as oxidant. The microreactor gave a better yield of 14% for phenol compared to 0.14% in the conventional laboratory scale reaction. Reaction conditions such as reaction time, reaction pH, and applied potential were optimized. With optimized reaction conditions selectivity of >37% and >88% conversion of benzene were obtained.

## 1. Introduction

The trend towards miniaturization has been driven by the need for fast, simple online measurements in environmental analysis and medical diagnostics. While initial studies were targeted at analytical applications, it has since been applied to synthetic chemistry in the form of microreactor [1–4]. The most interesting feature of microreactor is the large surface to volume ratio due to miniaturization [3, 5]. This gives microreactor excellent mass and heat transfer properties as compared to the conventional reaction vessels, thus allowing better temperature control and eliminating the risk of explosion [3, 6, 7]. Reactions can therefore be carried out under more aggressive conditions [3, 8]. The large increase of surface area in the microreactor is also beneficial for surface-catalyzed reactions. Furthermore, reactions can be influenced efficiently using potential rather than by heat [5]. Hence, reactions can be conducted at room temperature. Compared to conventional synthesis, the high degree of temperature control and high mixing efficiency in the microreactor also reduce side reactions and prevent thermal decomposition, leading to higher yield, selectivity, and purity under shorter time frame [1–7]. Microreactor also requires fewer reagents and produces less waste. This is cost efficient, safer, and beneficial to the environment [3, 8].

By connecting multiple microreactors, it is possible to prepare the exact amount of the chemical reagents required at the point of usage [8]. This minimizes the need to transport and store hazardous or unstable material. It is also possible to scale up production by repeating the same microreactor unit, thus enabling a cost-effective commercial production [3, 6, 7]. This approach would be particularly advantageous for the fine chemical and pharmaceutical industries, where productions are often in small amount [8, 9]. However, fabrication of the microreactor using photolithographic method requires clean room facilities and expensive instrumentation [10]. In addition, for heterogeneous catalysis, the technology is still immature due to the need for catalyst immobilization onto the channels. It is also susceptible to clogging failure and solvent incompatibilities [11].

Unlike photolithographic microreactor, the ordinary glass capillary reactor, fabricated for Suzuki coupling reactions [10] and the oxidation of glucose [11], is easily available, affordable, and easier to fabricate and handle. It consists of a glass capillary connected to a power supply and disposable plastic tips were used as sample reservoirs to introduce reactants and deploy electrodes. Phosphate buffer forms the base of the reaction mixture, as such little or no organic solvent is required. Reagents are driven through the capillary, using electroosmotic flow. The beauty of this glass capillary

microreactor lies in its simplicity. It has the advantages of its photolithographic counterpart. However, owing to its larger size and availability of porous catalyst, no immobilization of catalyst onto the capillary is required.

Phenol is an important raw material for the synthesis of chemicals, such as phenolic resin, E-caprolactam, and bisphenol A [12]. It was originally produced from toluene oxidation, followed by decarboxylation [13]. Nowadays, the toluene route is largely phased out due to low yield and high production cost. More than 90% of the world's phenol production is now based on the Cumene process. Developed between 1939 and 1945, it consists of three main reaction steps: (1) alkylation of benzene with propylene over an acid catalyst, (2) peroxidation of cumene, and (3) decomposition to phenol and acetone [13]. Acetone, as a coproduct, improves the overall economics of phenol production. However, as demand for phenol outgrows acetone, there is a possibility of oversupply of acetone. Therefore, direct oxidation of benzene to phenol which does not produce acetone as a byproduct is desired.

Many catalysts, including Fe, Cu, Pd, have been applied to the direct oxidation of benzene [14]. However, Ti based oxidation of benzene is not well studied [15]. The  $\text{TiO}_2$  nanoparticles are known to have intermediate properties between those of bulk and atomic or molecular structures. They are very interesting from the catalytic point of view, because of their high surface to volume ratio, which provides more accessible active sites for the oxidation reaction. However,  $\text{TiO}_2$  nanoparticles are rather kinetically unstable and they should be prevented from aggregation into larger particles. This was attributed to Ostwald ripening in which the small nanoparticles dissolve to form larger nanoparticles [16]. Therefore, for the first time, to improve the reaction efficiency, nanofiber membrane has been used as support to avoid the aggregation of nanoparticles during the reaction in capillary microreactor.

For the oxidation reactions most studies employed either hydrogen peroxide [17, 18] or oxygen gas [19, 20] as oxidant. Hydrogen peroxide is environmentally friendly as it leaves no hazardous residuals but oxygen and water after reaction. However, hydrogen peroxide is expensive and unstable [19]. Due to the small simple nature of the glass capillary microreactor, supply of oxygen gas via gas cylinder is also not viable. Therefore, we attempt to avoid these by in situ production of hydroxyl radical in the microreactor at the Pt electrodes with high potential.

## 2. Catalysts Preparation

$\text{TiO}_2$  is often used as catalyst for conventional oxidation [21] and photooxidation reactions [22]. In the latter experiment, the UV light enhances the decomposition of hydrogen peroxide by generating electron [23]. The  $\text{TiO}_2$  control the hydroxyl radical formation, thus improving the yield and selectivity for phenol. However, without  $\text{TiO}_2$ , excessive hydroxyl radicals were formed which would promote the further oxidation of benzene to hydroquinone, catechol (Scheme 1) [15].

However, in our initial studies with  $\text{TiO}_2$  nanoparticle in the microreactor, very low reaction efficiency of benzene was

resulted due to aggregation of  $\text{TiO}_2$  nanoparticles. Therefore,  $\text{TiO}_2$ -PVC nanofiber membrane was tested as catalyst for the oxidation reaction.  $\text{TiO}_2$ -supported polymer nanofiber with diameters down to a few nanometers was prepared by electrospinning process.

The  $\text{TiO}_2$  nanoparticles were synthesized based on the previously reported method [23], briefly, 14.17 mg of  $\text{TiI}_4$  was mixed with 25 mL of DMSO under constant magnetic stirring at ambient temperature, and then 1 mL of 0.1 M NaOH solution was added to the solution. The suspensions were centrifuged at 2500 rpm for 5 min and used for electrospinning process.

Electrospinning is a versatile electrostatic technique which can produce polymer nanofibers with high surface area. It involves the application of a high voltage to create an electric field between a droplet of polymer solution at the tip of a needle and a collector plate. A proper choice of processing parameters such as surface tension, viscosity, conductivity, concentration of the solutions, molecular weights, applied fields, and electrode configurations allows fibers with diameters down to a few nanometers to be produced.

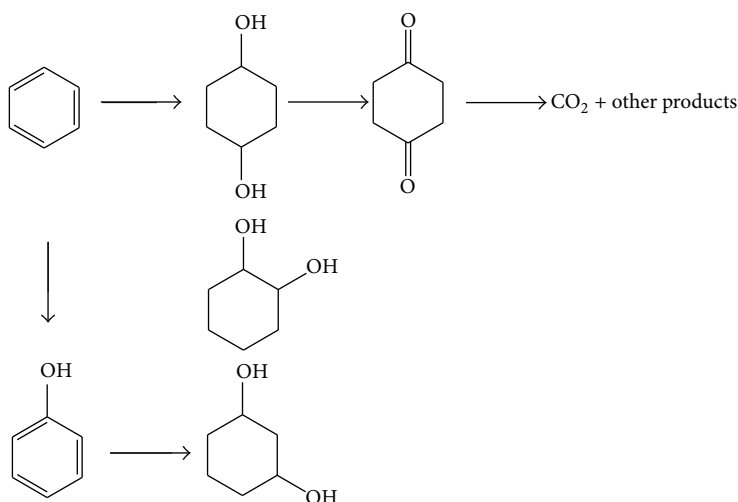
In our experimental setup for electrospinning, the tip-to-collector distance was kept at 8 cm. The flow rate of the polymer solution was held constant at 25.0  $\mu\text{L}/\text{min}$ , using a metering pump. The syringe had a capacity of 5 mL and the needle had an outside diameter of 0.8 mm. One electrode, capable of producing 30 kV was attached to the needle. The other electrode, was connected to the aluminum collector plate measuring 15 cm  $\times$  15 cm. 1.2 g (12 wt%) of PVC was blend in 100 mg of  $\text{TiO}_2$  in THF and sonicated for 12 hours. The solution of this polymer blend was electrospun on the aluminum foil at 25 kV and dried in air.

The morphology of the  $\text{TiO}_2$ -PVC nanofiber membrane was characterized by JEOL JSM 6701F scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) analyzer. SEM picture (Figure 1) showed that the membrane is porous, thus allowing EOF without the need to immobilize the catalyst onto the capillary. EDX spectrum shows that the nanofiber membrane has been supported with  $\text{TiO}_2$  nanoparticles.

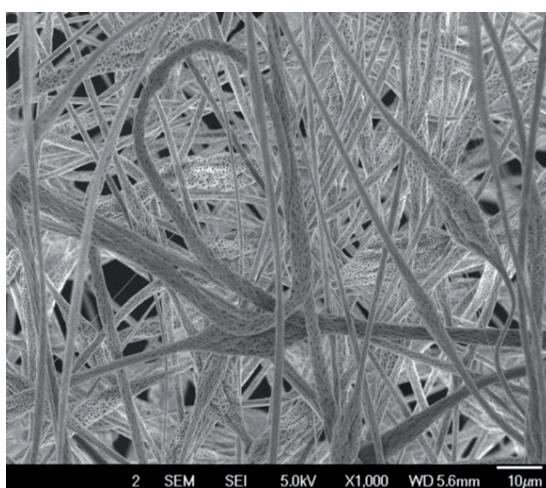
## 3. Capillary Microreactor and Oxidation of Benzene

The setup of the capillary microreactor is as shown in Figure 2. The capillary (0.5 mm internal diameter, 5 cm length) and the reservoirs were filled with 50 mM phosphate buffer solution. Disposable polypropylene pipette tips, inserted at both ends of the capillary, served as reservoirs. Care was taken to ensure the absence of air bubbles inside the capillary channel by ensuring constant current, to prevent back pressure which inhibits fluid flow. Platinum wires were used as the electrodes. All the reactions were monitored at room temperature and ambient pressure microreactor was rinsed with buffer followed by acetone and dried in between runs. Triplicate analyses were performed.

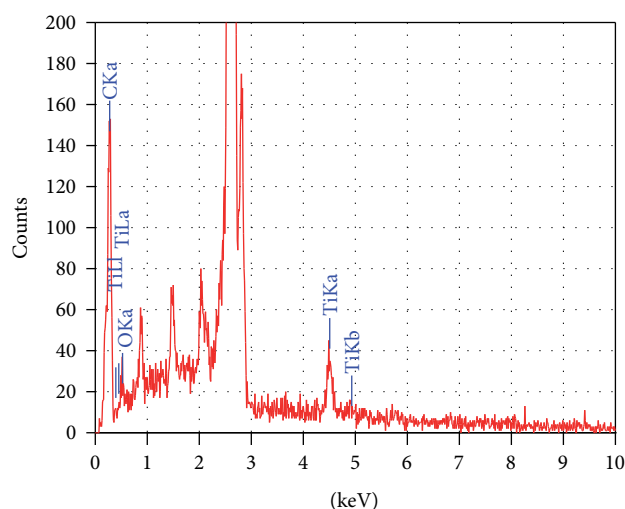
The capillary was filled with pH 2 phosphate buffer solution, and 6 pieces of  $\text{TiO}_2$ -PVC membrane (2  $\times$  2 mm



SCHEME 1: Proposed oxidation products of benzene.



(a)



(b)

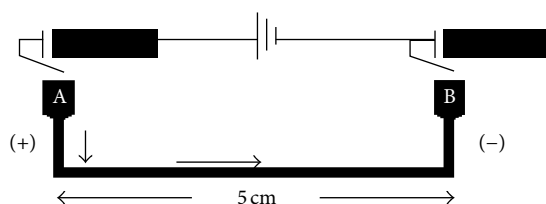
FIGURE 1: SEM picture (a) and EDX spectrum (b) of  $\text{TiO}_2$ -PVC nanofiber membrane.

FIGURE 2: Schematic diagram of capillary-microreactor. A and B are reservoirs (disposable pipette tips).

or approx. 1 mg) were placed in the channel. The  $\text{TiO}_2$ -PVC membrane was floating on the buffer solution. A  $50\ \mu\text{L}$  of benzene (100 mg/L) was added into reservoir A. A high-reaction potential of 2 kV was applied to reservoir A and B alternatively at 5 min intervals, and the other reservoir was connected to ground. The reaction was monitored for 10 min. The final solution was extracted with 1 mL of hexane:ethyl acetate (1:9) solvent.  $2\ \mu\text{L}$  of extract was then injected into

the GC-MS for analysis. Catalysts used were recovered and washed (ultrasonicated for 10 min) with ultrapure water and reused up to 10 cycles without compromising reaction efficiency.

Catalyst was introduced in the capillary channel and potential was applied alternatively in the reservoirs.

#### 4. Oxidation of Benzene in Conventional Scale Reaction

The hydroxylation of benzene by hydrogen peroxide was carried out using previously reported procedure [24]. Briefly, reaction performed in a  $150\ \text{cm}^3$  round bottomed flask at room temperature and ambient pressure with a high-speed stirrer at 600 rpm for 4 hours. In a typical experiment, approximately 100 mg of PVC- $\text{TiO}_2$  nanofiber membrane ( $2\ \text{mm} \times 2\ \text{mm}$ ) was added to a liquid mixture containing 60 mL of acetonitrile, 5 mL of  $\text{H}_2\text{O}_2$  (300 mg/L) and 5 mL

of benzene (100 mg/L). After the reaction, the mixture was extracted with hexane:ethylacetate (1:9 ratio) and then finally 2  $\mu$ L of extract was injected into the GC-MS for analysis.

## 5. Results and Discussion

The reactions were then optimized by varying various parameters, such as reaction time, applied potential, pH, and temperature, before comparison with the conventional laboratory scale reaction with the purpose to study the advantages of the microreactor. A control was performed without TiO<sub>2</sub>-PVC nanofiber membrane, and no phenol was detected in the reaction. Although there was no phenol formation, on average 50% of benzene was lost. Given that benzene is a volatile compound, the loss could be explained by vaporization under the open system and Joule heating from the applied potential. This loss is undesirable and illustrates that this microreactor is not very suitable for reaction involving volatile compounds.

In reaction process, it is necessary to determine the optimal reaction time. Oxidation of benzene to phenol using hydrogen peroxide in the conventional laboratory scale was typically performed for 4 hrs, with the best yields at 2.6% for the TiO<sub>2</sub> photocatalyst [24, 25]. Due to the volatility of the compounds and their trace amount, it is best to avoid extended time. The reaction time was studied between 5 and 30 min. The highest yield, 9.5%, for the microreactor was recorded at 10 min. Figure 3(a) shows that, beyond 10 min, hydroquinone and quinone peaks were observed. Therefore, subsequent reactions were run at 10 min reaction time.

The effect of applied potential on the reaction process was explored. Initial experiments were conducted without addition of potential to the benzene (only catalyst and buffer solution, the sample was ultrasonicated for 30 minutes) and no oxidation occurred.

The reaction potential was varied between 1 and 5 kV. It was observed that the conversion of benzene increases with increased applied potential (Figure 3(b)). This is consistent with the trends observed in other reactions [10, 11]. This can be explained by the increase in EOF in the capillary channel. For a glass microreactor, the capillary wall carries a negative charge, arising from ionization of the immobile silanol surface groups. This in turn attracts a diffuse layer of mobile cations. This diffuse layer migrates towards the more negative electrode when an electric field is applied [1]. The theoretical relationship between applied potential and EOF can be explained by the following equation. It can be seen that the greater the applied potential, the greater the EOF generated and thus the increased the reagents' mobility and the intensity of interaction between the reagent and the catalyst, leading to an enhancement in the reaction yield:

$$V_{\text{EOF}} = \frac{\zeta \epsilon E}{4\pi\eta}, \quad (1)$$

where  $\zeta$  is zeta potential,  $\epsilon$  is dielectric constant,  $E$  is applied potential, and  $\eta$  is viscosity of the buffer.

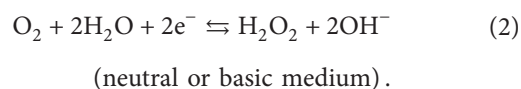
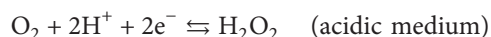
However, the yield of phenol showed a slight increase only up to 2 kV, followed by slight decrease for potential beyond 2 kV. A plausible explanation for such deviation from previously stated observations could be that the higher potential increased the rate of further oxidation for benzene and phenol. As such, there is no significant increase in the yield with respect to applied potential beyond 2 kV. At higher potential, formation of hydroquinone and quinone was observed which may explain a lower phenol yield. Therefore, 2 kV was chosen for subsequent experiments.

In addition, the applied potential may also induce electrochemical reactions, since the typical voltages used in EOF are over the potential required for an electrochemical reaction. Here, large amounts of hydroxyl radical (OH $\cdot$ ) can be produced during the electrolysis and participate in the oxidation of benzene. Applied potential can affect the rate of formation of hydroxyl radical and thus the overall rate of the oxidation of benzene. Our preliminary studies on without applied potential no phenol was obtained shows no sign of products. This indicates that oxygen source is required to produce benzene to phenol reaction. Application of high voltage to the buffer solution produces oxygen and free radical on the catalyst. This process facilitates the oxidation reaction.

Therefore, it could be useful to study the effect of applied potential on the kinetics of the reaction (this could be our interest of further research).

The effect of pH was investigated. Most papers published on oxidation of benzene to phenol are done at neutral or slightly acidic condition. Walling and Johnson (1975) found that, in Fenton's process, increasing the H<sup>+</sup> concentration decreases the yield of phenol due to the "inhibition" effect of H<sup>+</sup> ion in terms of the acid catalyzed dehydration of hydroxycyclohexadienyl radical to form cation radical, followed by its reduction with Fe(III) to give benzene [18]. Higher pH also leads to greater dissociation of Si-OH to Si-O<sup>-</sup>, giving larger zeta potential. This would in turn lead to greater EOF and larger yield. It was thus expected that higher pH would lead to higher conversion and yield.

However, the conversion and yield, which was significantly higher at pH 2, was observed to drop at pH 5 then increased at pH 7 and remained largely similar at pH beyond 7 (Figure 3(c)). This trend is similar to the effect of pH on the hydrogen peroxide production at Pt cathode, observed by Leng et al. [26]. This indicates that the conversion and yield of the reaction depends on the amount of hydrogen peroxide formed:



Hydrogen peroxide in situ formation is thus believed to be part of reaction scheme in the oxidation of benzene to phenol. Inhibition effect and EOF factor could still be present, but their effects are outweighed by the effect of pH on hydrogen peroxide in situ production. An optimized pH 2 was used for subsequent experiments.



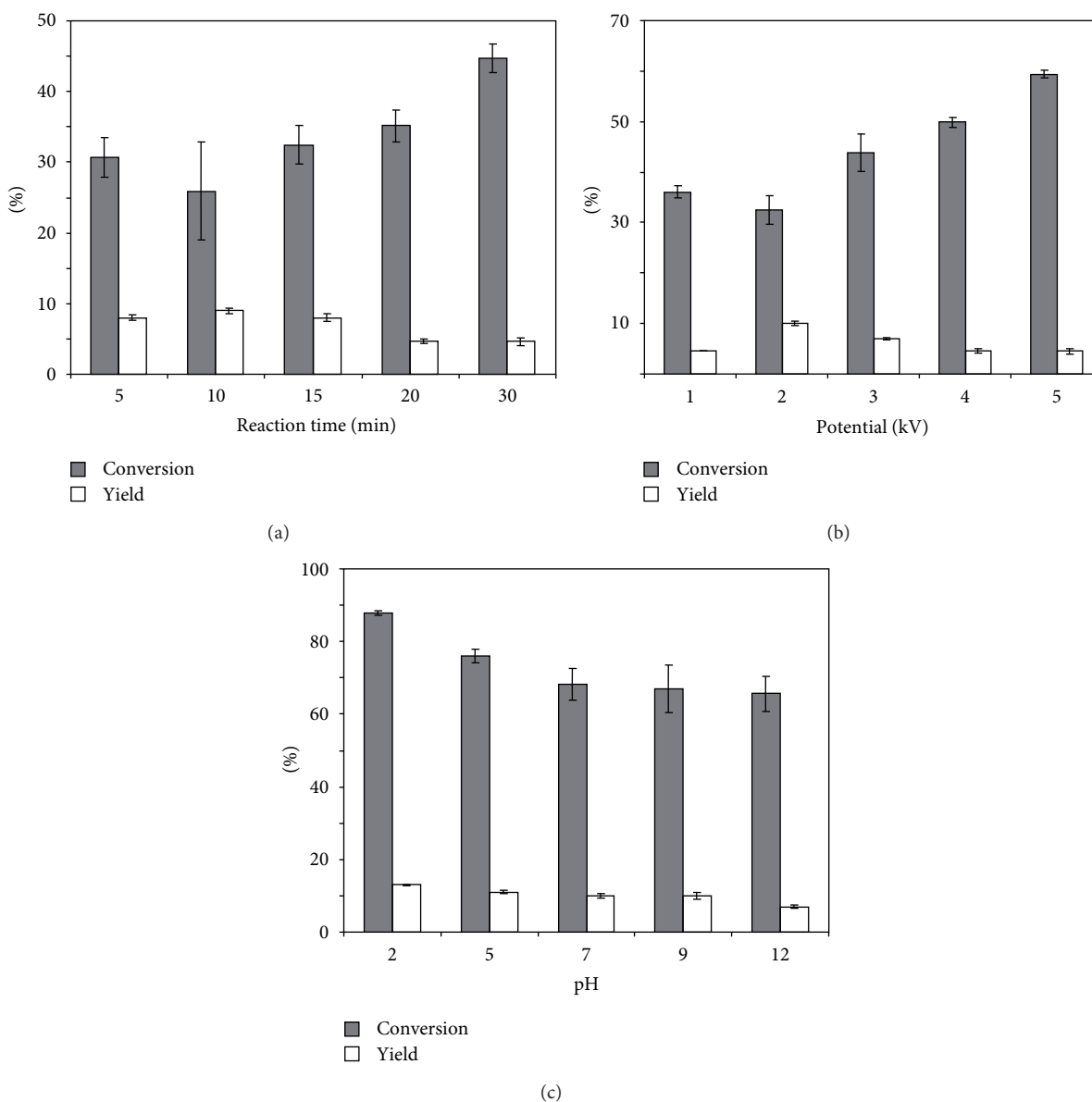


FIGURE 3: (a) Effect of reaction time in the capillary microreactor; reaction condition of 2 kV at pH 8. (b) Effect of different reaction potential in the capillary microreactor; reaction conditions, reaction pH 8, and reaction time 10 min. (c) Influence of different reaction pH in the capillary microreactor; reaction conditions, reaction time 10 min and applied potential of 2 kV.

From the control, it is apparent that a large amount of benzene is lost to volatilization unnecessarily. To reduce this lost, the setup was cooled in an ice bag throughout the experiment. This reduces the conversion and thus increases the selectivity and efficiency. However, at lower temperature, the reaction rate is slower, leading to lower yield. Therefore, room temperature was used for further optimization.

It is well known that, under the Fenton's process, hydrogen peroxide is reduced to give the hydroxyl radical, which subsequently attacks benzene to form phenol [18]. Besides ferrous ions, aromatic compounds can also undergo oxidation in the presence of metal ions such as  $\text{Cu}^+$ ,  $\text{Sn}^{2+}$ ,  $\text{Ti}^{3+}$ , which have a standard redox potential [19] of 0.15 V.

In the experiment only benzene,  $\text{TiO}_2$ -PVC nanofiber membrane catalyst, and phosphate buffer were used. The

application of high potential is used to promote the formation of radicals, instead of UV light. The effect of pH on the conversion and yield suggests that hydrogen peroxide in situ formation occurs. The hydrogen peroxide and  $\text{TiO}_2$ -PVC nanofiber membrane then formed the hydroxyl radical under high potential, which subsequently attacks the benzene to form phenol in a mechanism which is postulated to be similar to the Fenton's process.

## 6. Conventional Reaction

Oxidation of benzene using hydrogen peroxide was performed in the conventional manner and compared to the oxidation in the microreactor (Table 1). The conventional reaction yield (>1%) was lower than the capillary

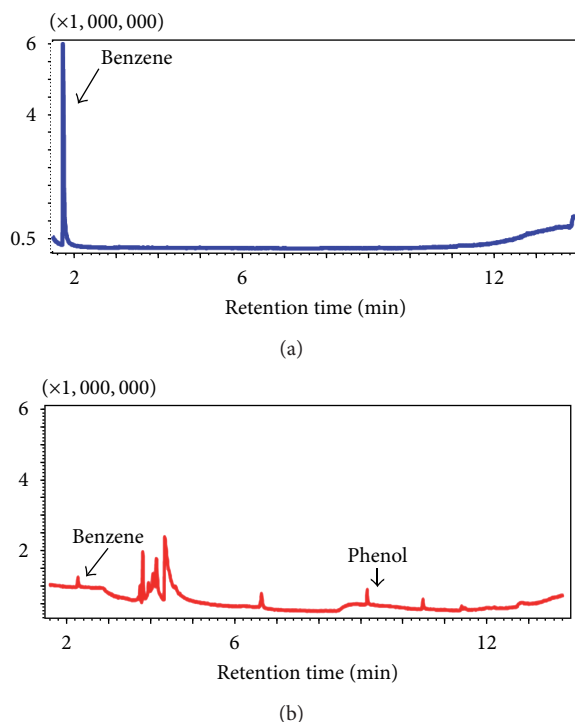


FIGURE 4: GC-MS reaction chromatogram of (a) 0 min and (b) after 30 min reaction time.

TABLE 1: Performance of oxidation of benzene in microreactor and conventional scale.

	Conversion (%)	Yield (%)	Selectivity (%)
Microreactor	88.5	14.2	37.0
Conventional	6.6	0.14	2.23

microreactor, whereas with optimized conditions using capillary microreactor, 88.5% conversion of phenol, 14.2% of yield, and 37.0% were obtained. However, reaction yield of microreactor study is comparable with the conventional scale reaction and is similar to those previously reported [24]. On the whole, the performance of the microreactor was far better than the conventional method, as expected due to the inherent properties of the microreactor. It was also achieved in a much shorter time with lesser chemicals used and no organic solvent. Figure 4 shows the GC-MS chromatogram of reaction time 0 min and 30 using capillary microreactor.

## 7. Conclusion

Oxidation of benzene, making use of the in situ production of hydrogen peroxide, was successfully conducted in a simple glass capillary microreactor under the presence of high applied potential and  $\text{TiO}_2$ -PVC nanofiber membrane as catalyst in acidic condition. We postulated that the oxidation reaction in the microreactor proceeds via a radical mechanism similar to the Fenton's process. The performance of  $\text{TiO}_2$ -PVC nanofiber membrane is better in the microreactor as compared to the conventional laboratory scale oxidation

reaction, in terms of the conversion, yield, and selectivity. In addition, the oxidation reaction using the microreactor can save time and cost. It is also environmentally friendly as no organic solvent was used during the reaction. Although the improved yield illustrated here is not good enough for industrial application, this paper has shown the usefulness of the microreactor as a testing tool for new catalyst and reaction.

## Acknowledgments

The National University of Singapore (NUS) is gratefully acknowledged for this work. The author thanks the Deanship of Scientific Research at King Fahd University of Petroleum and Minerals (Project no. SB111009).

## References

- [1] S. J. Haswell and P. Watts, "Green chemistry: synthesis in micro reactors," *Green Chemistry*, vol. 5, no. 2, pp. 240–249, 2003.
- [2] P. D. I. Fletcher, S. J. Haswell, E. Pombo-Villar et al., "Micro reactors: principles and applications in organic synthesis," *Tetrahedron*, vol. 58, no. 24, pp. 4735–4757, 2002.
- [3] M. Brivio, W. Verboom, and D. N. Reinhoudt, "Miniaturized continuous flow reaction vessels: influence on chemical reactions," *Lab on a Chip*, vol. 6, no. 3, pp. 329–344, 2006.
- [4] S. C. Jakeway, A. J. de Mello, and E. L. Russell, "Miniaturized total analysis systems for biological analysis," *Fresenius' Journal of Analytical Chemistry*, vol. 366, pp. 525–539, 2000.
- [5] H. Löwe and W. Ehrfeld, "State-of-the-art in microreaction technology: concepts, manufacturing and applications," *Electrochimica Acta*, vol. 44, no. 21, pp. 3679–3689, 1999.
- [6] Y. Kikutani, A. Hibara, K. Uchiyama, H. Hisamoto, M. Tokeshi, and T. Kitamori, "Pile-up glass microreactor," *Lab on a Chip*, vol. 2, no. 4, pp. 193–196, 2002.
- [7] C. Wiles, P. Watts, S. J. Haswell, and E. Pombo-Villar, "The application of microreactor technology for the synthesis of 1,2-azoles," *Organic Process Research and Development*, vol. 8, no. 1, pp. 28–32, 2004.
- [8] K. F. Jensen, "Microreaction engineering—is small better?" *Chemical Engineering Science*, vol. 56, pp. 293–303, 2001.
- [9] D. M. Roberge, L. Ducry, N. Bieler, P. Cretton, and B. Zimmermann, "Microreactor technology: a revolution for the fine chemical and pharmaceutical industries?" *Chemical Engineering and Technology*, vol. 28, no. 3, pp. 318–323, 2005.
- [10] C. Basheer, F. S. Jahir Hussain, H. K. Lee, and S. Valiyaveetil, "Design of a capillary-microreactor for efficient Suzuki coupling reactions," *Tetrahedron Letters*, vol. 45, no. 39, pp. 7297–7300, 2004.
- [11] C. Basheer, S. Swaminathan, H. K. Lee, and S. Valiyaveetil, "Development and application of a simple capillary-microreactor for oxidation of glucose with a porous gold catalyst," *Chemical Communications*, no. 3, pp. 409–410, 2005.
- [12] PERP Program, *Phenol/Acetone/Cumene News Report Alert*, Nexant ChemSystems, 2007.
- [13] R. Schmidt, "Industrial catalytic processes—phenol production," *Applied Catalysis A*, vol. 280, no. 1, pp. 89–103, 2005.
- [14] G. Tanarungsun, W. Kiatkittipong, S. Assabumrungrat, H. Yamada, T. Tagawa, and P. Praserttham, "Multi transition metal catalysts supported on  $\text{TiO}_2$  for hydroxylation of benzene

- to phenol with hydrogen peroxide," *Journal of Industrial and Engineering Chemistry*, vol. 13, no. 5, pp. 870–877, 2007.
- [15] R. T. S. Oliveira, G. R. Salazar-Banda, M. C. Santos et al., "Electrochemical oxidation of benzene on boron-doped diamond electrodes," *Chemosphere*, vol. 66, no. 11, pp. 2152–2158, 2007.
- [16] Y. Li, E. Boone, and M. A. El-Sayed, "Size effects of PVP-Pd nanoparticles on the catalytic Suzuki reactions in aqueous solution," *Langmuir*, vol. 18, no. 12, pp. 4921–4925, 2002.
- [17] T. Mizuno, H. Yamada, T. Tagawa, and S. Goto, "Partial oxidation of benzene in benzene-water bi-phase system," *Journal of Chemical Engineering of Japan*, vol. 38, no. 10, pp. 849–853, 2005.
- [18] C. Walling and R. A. Johnson, "Fenton's reagent. V. Hydroxylation and side-chain cleavage of aromatics," *Journal of the American Chemical Society*, vol. 97, no. 2, pp. 363–367, 1975.
- [19] Y. Wu, M. Xing, J. Zhang, and F. Chen, "Effective visible light-active boron and carbon modified TiO<sub>2</sub> photocatalyst for degradation of organic pollutant," *Applied Catalysis B*, vol. 97, no. 1-2, pp. 182–189, 2010.
- [20] A. Kunai, S. Hata, S. Ito, and K. Sasaki, "Mechanistic study of air oxidation of benzene in sulfuric acid catalyzed by cuprous ions," *Journal of Organic Chemistry*, vol. 51, no. 18, pp. 3471–3474, 1986.
- [21] A. Kachina, S. Preis, and J. Kallas, "Catalytic TiO<sub>2</sub> oxidation of ethanethiol for environmentally benign air pollution control of sulphur compounds," *Environmental Chemistry Letters*, vol. 4, no. 2, pp. 107–110, 2006.
- [22] V. Ramaswamy, P. Awati, and A. V. Ramaswamy, "Epoxidation of indene and cyclooctene on nanocrystalline anatase titania catalyst," *Topics in Catalysis*, vol. 38, no. 4, pp. 251–259, 2006.
- [23] I. Zumeta, D. Díaz, and P. Santiago, "Synthesis of TiO<sub>2</sub> nanoparticles with narrow size distribution and their evaluation in the photocatalytic oxidative degradation of bis(4-nitrophenyl) phosphate," *Journal of Physical Chemistry C*, vol. 114, no. 26, pp. 11381–11389, 2010.
- [24] G. Tanarungsun, W. Kiatkittipong, S. Assabumrungrat, H. Yamada, T. Tagawa, and P. Praserttham, "Fe(III), Cu(II), V(V)/TiO<sub>2</sub> for hydroxylation of benzene to phenol with hydrogen peroxide at room temperature," *Journal of Chemical Engineering of Japan*, vol. 40, no. 5, pp. 415–421, 2007.
- [25] H. Park and W. Choi, "Photocatalytic conversion of benzene to phenol using pure and modified TiO<sub>2</sub>," *Catalysis Today*, vol. 101, pp. 291–297, 2005.
- [26] W. H. Leng, W. C. Zhu, J. Ni, Z. Zhang, J. Q. Zhang, and C. N. Cao, "Photocatalytic destruction of organic using TiO<sub>2</sub> as a photoanode with simultaneous production of H<sub>2</sub>O<sub>2</sub> at the cathode," *Applied Catalysis A*, vol. 300, pp. 24–35, 2006.

