KKU ENGINEERING JOURNAL October–December 2014;41(4):421-426 Research Article

KKU Engineering Journal

http://www.en.kku.ac.th/enjournal/th/

The effects of HNO_3 and CH_3COOH on the aqueous phase hydroxylation of benzene to phenol by hydrogen peroxide over TS-1 catalyst

Yaowaluk Chankeaw, Rudemas Manosak and Tharathon Mongkhonsi *

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok Thailand, 10330.

Received January 2014

Accepted June 2014

Abstract

The direct synthesis of phenol by benzene hydroxylation with hydrogen peroxide over titanium silicalite-1 (TS-1) catalyst is carried out in a three phase stainless steel reactor system. The effects of HNO_3 and CH_3COOH on the concentration are studied. It was found that the adding of HNO_3 and CH_3COOH could enhance the conversion of benzene to phenol. The concentration that of HNO_3 also affects extend of the reaction.

Keywords : Hydroxylation, Benzene, Phenol, TS-1

---

* Corresponding author.

Email address: tharathon.m@gmail.com

1. Introduction

Phenol is widely used for raw material of many materials. In industrial scale, the majority of phenol comes from cumene process. However, the cumene process comprises of several reaction steps. Firstly, benzene reacts with propylene to form cumene. Later, the cumene is oxidized by O_2 to cumene hydroperoxide. Finally, cumene hydroperoxide is decomposed by acid to produce phenol and acetone. A new process having fewer reaction steps is thus required.

One reaction of most interest for industrial scale is the direct hydroxylation of benzene to phenol with hydrogen peroxide [1-4] using TS-1 catalyst under mild condition. This reaction can synthesize phenol from benzene in only one reaction step.

A problem with the direct benzene oxidation is the reactants, benzene and hydrogen peroxide, are immiscible liquid which benzene is on the surface of the hydrogen peroxide phase while the catalyst stayed at the bottom of the reactor. This results in low conversion of reactant. In one of our research [6] we have found that a better way than using solvent is to operate the reactor in the three phase system but increase the system temperature. The increase temperature leads to higher amount of benzene dissolves in the aqueous phase. This leads to higher benzene conversion. [7] In another subsequence work we attempted to increase the solubility of toluene in water by adding some HCl and found that increase acidity of the aqueous solvent can increase the conversion of toluene to benzaldehyde by H_2O_2 using the same reactor system as in the present work. Therefore, this work attempted to apply the knowledge of using acid to increase conversion with our benzene + H_2O_2 system.

2. Research Methodology

2.1 The preparation of the TS-1 catalyst

TS-1 catalyst is prepared by hydrothermal method which the mixture of gel and decant solution. [5] For the gel solution, 51.95 g of NaCl, 2.29 g of $Ti[O(CH_2)_3CH_3]_4$, 7.88 g of TPABr, 2.39 g of NaOH and 4.95 ml of H_2SO_4 was added to 268 ml of de-ionized water. Next, solution of sodium silicate is added dropwise to control the pH of the solution and maintain the pH to be within the range 9-11. Then the gel mixture is centrifuged for 15 minutes to separate the formed gel from the supernatant liquid. The precipitated gel mixture is milled for 15 minutes. For the decant solution, 26.27 g of NaCl, 2.29 g of $Ti [O(CH_2)_3CH_3]_4$ 7.53g of TPABr and 3.4 ml of H_2SO_4. H_2SO_4 is added to 164 ml of de-ionized water. Then, solution of sodium silicate is added drop wise. The colorless supernatant liquid is separated from the mixture by centrifugation. The supernatant of the decant solution are filled in an autoclave which is pressurized to 3 barg by nitrogen gas and heated up to 180°C. The autoclave temperature is maintained at this temperature for 3 days. The crystals are calcined at 550°C in air stream for 7 hr.

2.2 The characterization of the TS-1 catalyst

Crystal structure of the catalysts are performed by X-ray diffraction (XRD) technique with a SIEMENS D5000 using CuKα radiation with Ni filter over the from 6° to 30° with step size 0.04°/sec.

Catalyst composition is determined by x-ray fluorescence spectroscopy (XRF). The analysis is carried out on Siemens SRS3400.

N_2 – physisorption method (BET) is used to determine total surface area. The measurement is conducted by Micromeritrics ASAP 2020.

Infrared absorption is carried out on a Thermo Nicolet (FT-IR) model 6700. The measurement is performed in transmission mode.

2.3 The solubility of benzene

The solubility of benzene in acidic aqueous solutions was determined at room temperature. In each experiment 160 ml of acidic aqueous solution (0.05M, 0.1M, or 0.15M of nitric acid solutions) is added into a 250 ml beaker. Then a ¼ inch OD stainless steel tube was vertically placed in the reactor. This tube acts as a sampling well. Then a volume of benzene which must be high enough to completely cover the overall top surface of the aqueous throughout of experiment was added. Then the mixture was stirred. At a specified interval, a small volume of the aqueous phase was sampled from the vertically placed tube to measure the concentration of dissolve benzene in the aqueous phase. The collected samples are analyzed by a Shimadzu GC8A gas chromatograph equipped with a FID and GP10% SP2100 to measure the concentration of benzene.

2.4 The hydroxylation of benzene

The hydroxylation reaction of benzene to phenol with hydrogen peroxide was carried out in a 150 ml stainless steel SS304 reactor. 1 g of catalyst is loaded and filled with 120 ml of water or acidic aqueous solution into the reactor. Then 8.9 ml of benzene is filled into the reactor. After that, the reactor is sealed and pressurized to 2 barg with nitrogen gas and placed in an oil bath for heating up to 70°C and hold on at this temperature for 1 hour to remove gas from pores of the catalyst. Next, 1 ml of H_2O_2 (30%w/v) is injected into the reactor. The reaction is carried out for 2 hours and then reactor is cooled down to stop the reaction by placing the reactor into an ice bath. Finally, 100ml of ethanol is added into the reactor. The products are analyzed by a Shimadzu GC8A gas chromatograph with FID and GP10% SP2100. The temperature of the oven is programmed to increase from 80 °C to 230°C with a heating rate of 5 °C/min.

3. Research Results and Discussion

3.1 Characterization of catalyst

The surface area of the catalyst measured by BET method was found to be 383.1 m^2/g. The %wtof Ti and Si was found to be 1.62 and 97.03, respectively. The x-ray diffraction (XRD) showed in Figure 2 showed the typical diffraction pattern of the MFI structure (2 = 7.9, 8.8, 14.8, 23.9 and 24.4) [6-9]. The functional group analyzed using FT-IR showed in Figure 3 shows the absorption band around 960 cm^{-1}. This confirms that Ti^{4+} had entered a silica lattice.

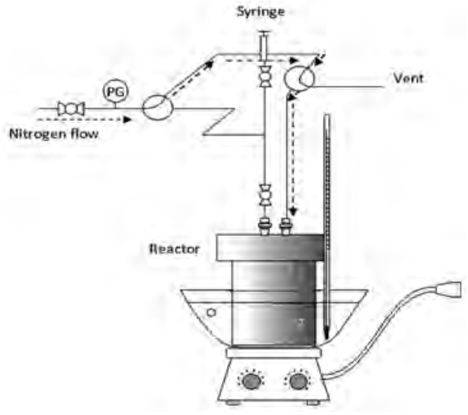

Figure 1 Schematic diagram of the reactor system

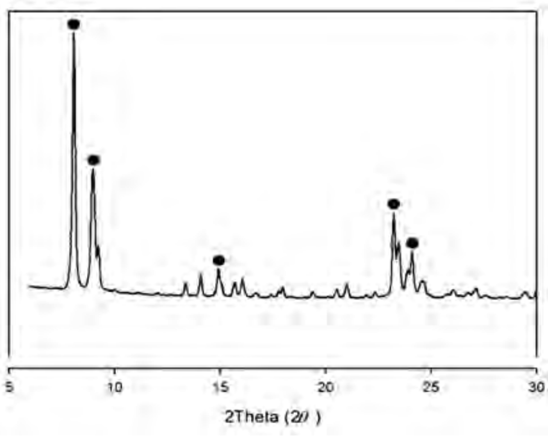

Figure 2 The XRD pattern of TS-1

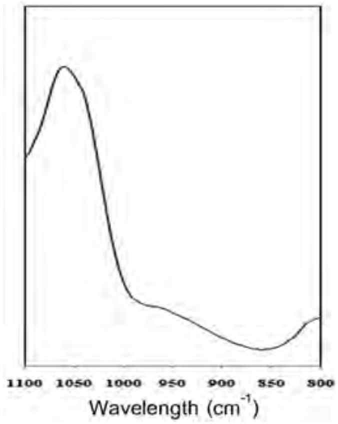

Figure 3 The FT-IR spectra of TS-1

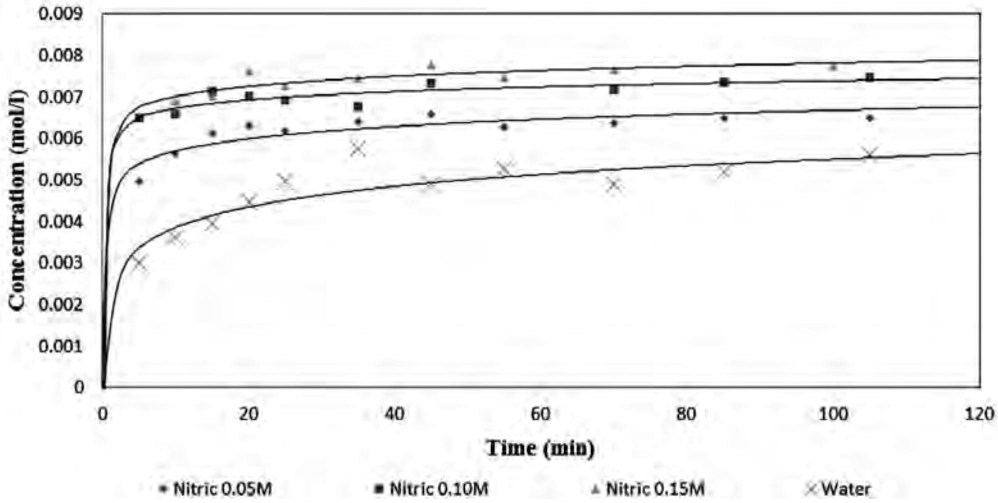

Figure 4 The concentration of benzene in aqueous phase versus time. Conditions : Room temperature, 250 ml of beaker, benzene covered on 160 ml of solution

3.2 The effect of nitric acid and acetic acid on the hydroxylation of benzene

The results in Table 1 shows the effects of nitric acid and acetic acid of solution on the H_2O_2 conversion to phenol. The results clearly show that the addition of acids significantly increase the conversion of H_2O_2 to phenol. In the next step the effect of concentration of nitric acid was studied. Acetic acid is not used because H_2O_2 may react with the acetate ion that can decrease amount of H_2O_2. [9]

$$CH_3COOH + H_2O_2 \longleftrightarrow CH_3COOOH + H_2O \quad (1)$$

The results obtained from using different concentration of nitric acid was reported in Table 2.

Figure 4 shows the concentration of benzene in aqueous phase versus time. It was found that higher concentration of HNO_3 results in higher concentration of benzene dissolved into the aqueous phase.

The results in Table 2 shows that there was an optimal concentration of nitric acid to achieve the highest H_2O_2 conversion at 0.01 M HNO_3 and the conversion of H_2O_2 can drop when excessive amount of nitric acid was used. Too low acid concentration results in low concentration of benzene in the aqueous phase. Too high acid concentration results in too high benzene concentration in the aqueous phase. The excessive amount of benzene in the aqueous phase will cover the catalyst surface. Lead to the prohibiting of H_2O_2 molecule from reaching the catalyst surface. Therefore, the conversion of H_2O_2 can drop when excessive amount of nitric acid is used..

Table 1 The effects of nitric acid and acetic acid of solution on the H_2O_2

Reaction conditions: 0.01 mol of benzene and 0.01mol of H_2O_2, 1 g of TS-1 catalyst 120 ml of solution, reaction time 2 hours, temperature 70°C and pressure 2 barg

Solution	Concentration (mol/L)	H_2O_2 conversion
Water	-	11.23
Nitric acid	0.1	14.93
Acetic acid	0.1	17.53

Table 2 The effects of different concentration of nitric acid

Reaction conditions: 0.01 mol of benzene and 0.01mol of H_2O_2, 1 g of TS-1 catalyst 120 ml of solution, reaction time 2 hours, temperature 70°C and pressure 2 barg

Solution	Concentration (mol/L)	H_2O_2 conversion
Nitric acid	0.05	13.19
	0.10	14.93
	0.15	14.60

4. Conclusion

In the present work, the addition of nitric and acetic acids increases the solubility of benzene in aqueous phase. The higher concentration of benzene in the aqueous phase can increase the conversion of H_2O_2 to phenol. Too high concentration of benzene in the aqueous, however, leads to lower H_2O_2 conversion.

5. References

[1] Ricci M, Bianchi D, Bartolo R in: Cavani F, Centi G, Perathoner S, Trifirò F (Eds.), Sustainable Industrial Chemistry. Principles, Tools and Industrial Industrial Examples, Wiley-VCH, Weinheim, 2009;507-28.

[2] Clerici MG, Top. Catal 2001;(15):257-63.

[3] Centi G, Perathoner S, Catal. Today 2009;(143):145-50.

[4] Perego C, Carati A, Ingallina P, Mantegazza MA, Bellussi G, Appl. Catal. A 2001;(221): 63-72.

[5] Manosak R. Effect of ions on the hydroxylation of benzene to phenol by hydrogen peroxide over TS-1 catalyst, Master's Thesis, Chulalongkorn University, Bangkok, 2011.

[6] Mitpapan S. Benzene hydroxylation by hydrogen peroxide at elevated temperature over titanium silicalite-1 catalyst. Pathumwan Academic Journal 2010;1(2):5-10.

[7] Kasemsukphaisan N. Effect of acidity of solution on reaction between toluene and hydrogen peroxide over TS-1 catalysts, Master's Thesis, Chulalongkorn University, Bangkok, 2009.

[8] Taramasso M, Perego G, Notari B. Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides. United State Patent US 4,410,501. 1983 Oct 18.