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Contributed Paper

Catalytic Activity of TS-1 on the Hydroxylation of Benzene and Toluene with Hydrogen Peroxide in a Bubble Reactor

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ABSTRACT

The hydroxylation of benzene with hydrogen peroxide as an oxidant over TS-1 was carried out in a bubble reactor. The catalyst was prepared by hydrothermal synthesis. When the volume of benzene feeding in each period was increased while the feeding frequency constant, the conversion of benzene decreased. The amount of phenol increased when the reaction mixture was left for a period of time up to 4 hours, suggesting the reaction of benzene dissolved in the liquid phase. The extension of the experiment on the hydroxylation of toluene using the best condition obtained from the hydroxylation of benzene shows that o-cresol and p-cresol are two main hydroxylation products of toluene.

Keywords: Hydroxylation, Benzene, Toluene, Titanium silicalite-1.

1. INTRODUCTION

Phenol has been in production since the 1860s. One of the early uses for phenol was as an antiseptic. Towards the end of the 19th century, industrial scientists found new uses for phenol in the synthesis of dyes, aspirin, picric acid and one of the first high explosives. Afterwards, it was found that phenol could be condensed with aldehydes to make resinous compounds, a process still in use today. Besides, Phenol is also used to make chemical intermediates [1] for a wide range of other applications, ranging from plastics to pharmaceuticals and agricultural chemicals.

Presently, phenol is produced by the three

stage cumene method that has several significant shortcomings such as the intermediate hydroperoxide is explosive, ecological problems, and the production rate of the co-product acetone exceeds market demand. Therefore, there are intensive searches for a better route to produce phenol based on the direct benzene oxidation. One of the such route is the hydroxylation of benzene using hydrogen peroxide to phenol over titanium silicalite-1 (TS-1). Since, TS-1 has unique catalytic properties [2], being effective in the oxidation of a variety of organic compounds at low temperature [3,4],

many researchers have attempted to improve phenol productivity by improving catalytic activity of the TS-1 and/or mode of reactor operation [4-8].

Naturally, the surface of TS-1 prefers the adsorption of a non-polar species. The hydroxylation of benzene by H_2O_2 , however, requires the presence of both benzene and H_2O_2 on the TS-1 surface. If the hydroxylation is performed in liquid phase, the catalyst surface is mostly covered by the adsorbed benzene and left only a small area for H_2O_2 to present on the catalyst surface. The consequence is low reaction rate.

In the present work, an attempt has been made to enhance the adsorption of H_2O_2 by changing benzene feeding method. The catalyst is firstly dispersed in H_2O_2 in a slurry form to allow H_2O_2 to be the first species that cover the catalyst surface. Then, benzene vapor is bubble through the slurry. Due to the concentration of benzene is reduced and benzene is introduced secondly, the portion of the catalyst surface covered by H_2O_2 is expected to be higher than feeding benzene in liquid phase.

Although, the hydroxylation of benzene to phenol, catalyzed by TS-1 using hydrogen peroxide as an oxidant, have been studied extensively, very little know about hydroxylation of benzene and alkylbenzene (toluene and ethylbenzene). In this work, TS-1 and metal modified TS-1 are studied in the hydroxylation of benzene and extension to alkylbenzene in a bubble reactor with hydrogen peroxide as an oxidant.

2. MATERIALS AND METHODS

2.1 Catalyst preparation

The TS-1 catalyst were prepared by hydrothermal method using sodium silicate and titanium(IV)butoxide as silicon and titanium source, respectively. Tetrapropylammonium bromide (TPABr) was used

as organic template. The atomic ratio of Silicon/Titanium in the preparing solutions was set at 50. The pH of the gel mixture was maintained within the range 9-11. H_2SO_4 (conc.) or NaOH solution were used to adjust the pH of the gel mixture to be in the appropriate level if it was necessary. A decantation solution was prepared same as for the preparation of gel mixture. However, before mixing, the pH of the solution was adjusted to be between 9-11. The mixture was placed in a stainless steel autoclave. The atmosphere in the autoclave was replaced with nitrogen gas and pressurized up to 3 kg/cm² gauge. Then, the autoclave was heated from room temperature to 160 °C with a heating rate of 2 °C/min, and then heating up to 210 °C with a heating rate of 12 °C/h while being stirred at 60 rpm, followed by cooling the mixture to room temperature in the autoclave overnight. The product crystals were washed with de-ionized water until the pH value of the washing water decrease from 10 to 7. Then, the crystals were dried in an oven at 110 °C for at least 24 h. The dry crystals were calcined in an air stream at 550 °C and held at that temperature for 7 h, by heating them from room temperature to 550 °C at a heating rate of 8.6 °C/min to burn off the organic template that leave the cavities and channels in the crystals. The calcined crystals were finally cooled down to room temperature and stored in a dessicator. Before using, the catalysts were immersed in a 5M HNO_3 aqueous solution for 3 hours, then wash with water. Finally the catalysts were calcined again at 540 °C for 7 h in static air.

2.2 Characterization

The chemical composition analysis of the catalyst was performed by X-ray fluorescence (XRF) Siemens SRS3400. The surface area and total pore volume of catalyst were measured by BET Micromeritics ASAP 2020

using N_2 adsorption method. The crystallinity and X-ray diffraction patterns of the catalysts were performed by an X-ray diffractometer SIEMENS D5000 using Cu K α radiation with Ni filter. The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. The acidic properties of the catalysts were determined by pyridine adsorption and temperature programmed desorption of ammonia (NH_3 -TPD).

2.3 Hydroxylation reaction

The hydroxylation of benzene was carried out in a bubble reactor. The reactor was immersed in an oil bath in order to make the working temperature constant and

performed at atmospheric pressure. Typically, 1 g of catalyst and 40 ml of 30% H_2O_2 were added into reactor without any organic solvent. The reaction mixture was stirred by a magnetic bar to disperse the catalyst. Then, benzene liquid was pulse-injected to the system (0.05 ml, 0.1 ml or 0.2 ml, depends on the experiment) at the interval of 1, 2, 4 or 8 minutes (depends on the experiment). The reaction was carried out for 0.5, 1, 2 or 4 hours. The best result obtained from benzene was used for the hydroxylation of toluene. Reaction products were analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A) and GP 10% SP-2100 as a packed column.

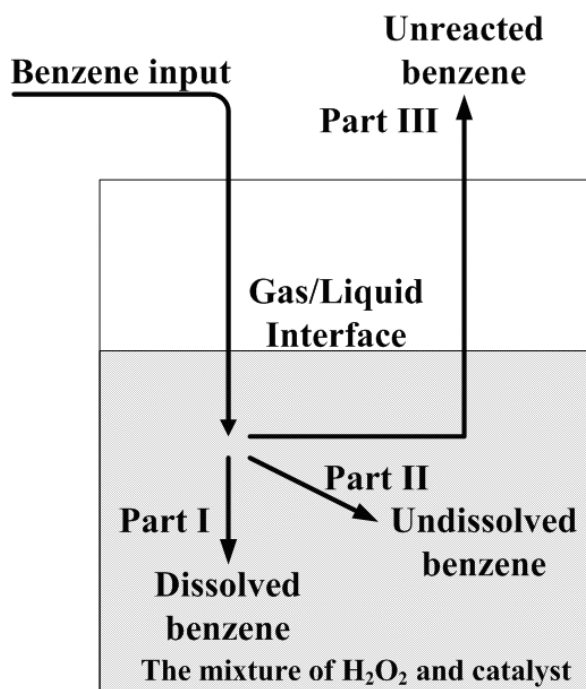


Figure 1. The model for the hydroxylation of benzene in the bubble reactor.

In the model, the gaseous benzene which enters the reactor is separated into 3 parts; Part I dissolve in H_2O_2 , Part II non-dissolve in H_2O_2 and Part III leave the system without reacting. Benzene in Part I is benzene molecules

that enter the reactor and dissolve in the H_2O_2 phase. Benzene molecules in this part may further react with H_2O_2 to form phenol product. Nevertheless, the amount of benzene in this part is very low due to the

low solubility of benzene in water. Therefore, the hydroxylation reaction in this part is low. Benzene in part II is benzene molecules that enter to the reactor and stay in the H_2O_2 phase in bubble form. The benzene bubble will float up from the bottom of the reactor to the gas/liquid interface. During the path way, benzene bubble will have an opportunity to interact with H_2O_2 and the catalyst. The

reaction will take place and the phenol product will be formed. The benzene molecules which do not react with H_2O_2 will leave the system as propose in part III.

3. RESULTS AND DISCUSSION

3.1 Feeding procedure

3.1.1 Effect of volume of benzene feeding per period

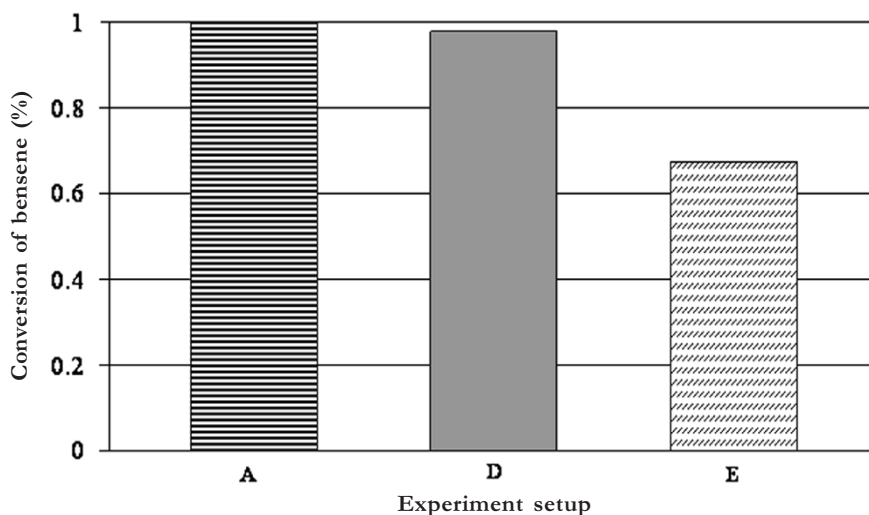


Figure 2. The effect of the amount of benzene feeding per period on the conversion of benzene. (A: Injected benzene 0.05 ml in each 2 minutes, D: Injected benzene 0.1 ml in each 2 minutes, E: Injected benzene 0.2 ml in each 2 minutes)

The results in Figure 2 show that conversion of benzene decreased when the volume of benzene feeding in each period increase. This behavior could be explain by model in Fig. 1 that when large amount of benzene was fed while the solubility rate of benzene did not increase proportionately to the volume of benzene injected in each injection, the benzene molecule which did not dissolve into the H_2O_2 phase would leave the reactor

In this case, the rate determining step could be the reaction of benzene to produce phenol. To better understand about the rate determining step, the average mole of phenol produced in each period was calculated as shown in Table 1.

From Table 1, the calculation data exhibit that the average mole of phenol produced in each period increased when the amount of benzene feeding increased. It might suggest that the increment of the amount of benzene feeding would increase the diffusion of benzene molecule to the catalyst active site resulted in the increasing of mole phenol produced in each period. Hence, the rate determining step should be the diffusion of benzene to the active site. However, the increment of phenol production was not in proportionate with the increment of benzene amount (i.e. between D and E, the amount of benzene increased two times but the phenol produced increased slightly). It seems that if

further increase the amount of benzene, the phenol production would become steady. In this point, the rate determining step would change from the diffusion of benzene molecule to the reaction of benzene to phenol on the active site.

Table 1. The calculation data of average mole of phenol produced in each period.

Benzene feeding in each period (ml/2minutes)	Number of benzene injection ⁺	Overall benzene conversion (%)	Overall mole of phenol produced (mole)	Average mole of phenol produced in each period (mole)*
0.05 (A)	60	1.00	0.00034	5.64×10^{-6}
0.1 (D)	30	0.98	0.00033	1.10×10^{-5}
0.2 (E)	15	0.67	0.00023	1.51×10^{-5}

⁺ The number of benzene injection in each experiment was differenced because the volume of benzene feeding in each period was varied, but the overall volume of benzene feeding was fixed at 3 ml.

*The value in table was obtained from dividing overall mole of phenol by number of benzene injection.

3.1.2 Effect of benzene feeding period

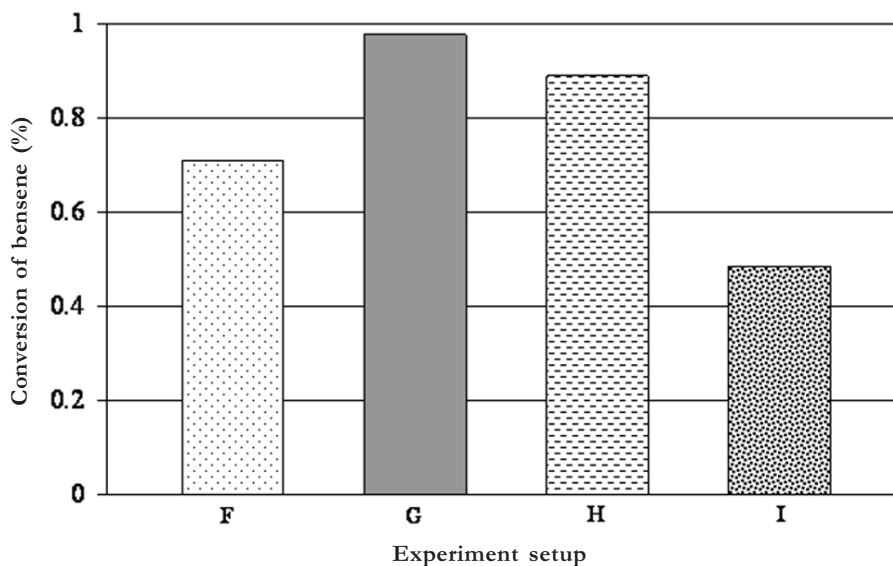


Figure 3. The effect of benzene feeding period on the conversion of benzene (F: Injected benzene 0.1 ml in each 1 minutes, G: Injected benzene 0.1 ml in each 2 minutes, H: Injected benzene 0.1 ml in each 4 minutes, I: Injected benzene 0.1 ml in each 8 minutes).

From Figure 3, it shows that the conversion increased when increased the feeding period from 1 to 2 minutes and then dropped continuously with further increasing benzene feeding period. The results of set F and G show that benzene feeding at higher frequency is less the benzene conversion than the feeding lower frequency. Consider the model from Fig. 1, the benzene in reactor was separated in the 3 parts. When the volume of benzene was fed at very high frequency, the gaseous benzene in the reactor was more than enough. In part I, the amount of benzene was limited by solubility of benzene in water therefore the trend of the amount of benzene was constant. Due to the hydroxylation reaction was slowly, the excess benzene is unable to conduct the reactions in part II. The unnecessary benzene will leave the reactor as in part III. Hence, set F driving force is higher than the ability of reaction and benzene to dissolve in the H_2O_2 phase cause to low benzene conversion.

Considering benzene feeding in our

investigated region, the optimum condition was found at 2 minutes feeding period. When the feeding period was more than 2 minutes, it was observed that the conversion decreased. The decrement of conversion may be because of competitive adsorption between benzene reactant and phenol product on the catalyst surface. An amount of benzene must present in the H_2O_2 phase to counter balance the adsorption of phenol, which is stronger adsorbed on the catalyst surface. The concentration of benzene in the H_2O_2 phase is allowed to low (i.e. the time interval between each injection is increased), more phenol will be adsorbed on the catalyst surface, thus, leaving less active site for the benzene. To better understand about the phenol adsorption into the catalyst, the expandable experiment is the effect of catalyst immerses the phenol solution. The phenol solution without catalyst and with catalyst were examined the disappearance of phenol in the solution.

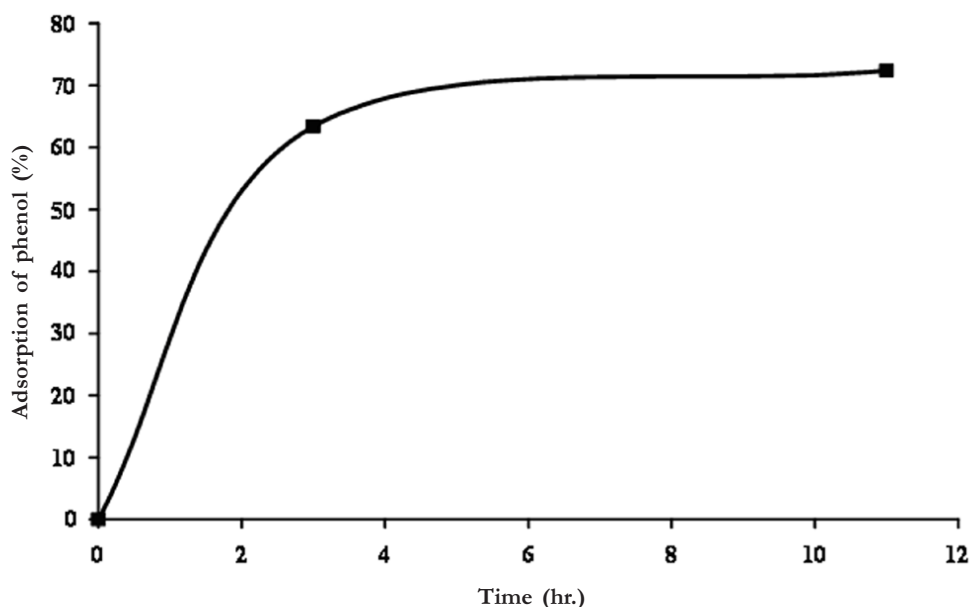


Figure 4. The adsorption of phenol on TS-1 catalysts.

Figure 4 elucidates that the catalyst could adsorb phenol on its surface. The reason of low benzene conversion, set H and I, is the phenol adsorption on the catalyst surface blocked the active site of the catalysts.

Finally, these experiments could confirm that the pulse feeding method in our condition should make the appropriate flow of benzene in the reactor. The optimum feeding conditions which gave the highest conversion was the amount of benzene feeding at 0.1 ml injected in each 2 minutes.

3.2 Effect of reaction time

Mole of phenol produced in difference reaction time was measured in order to optimize the condition which gives the highest catalytic activity. Fig. 5 demonstrates that the amount of phenol increased when the

experiments were left at the long time. Considering the reaction rate from the slope of graph, it was found that the slope of graph decreased slowly when the reaction time increased. It could predict that the trend of phenol produced would converge to constant value when reaction time was higher than 4 hours. After 4 hours, the catalyst might be inactive and would not be able to produce phenol anymore. Thus, this phenomenon might be because of the competitive adsorption of water on the catalyst active site. The reaction would occur only when the catalyst was not fully absorbed by water molecules. When the catalyst was fully absorbed, benzene molecule would not have the chance to reach active site of the catalyst and the hydroxylation reaction would be limited.

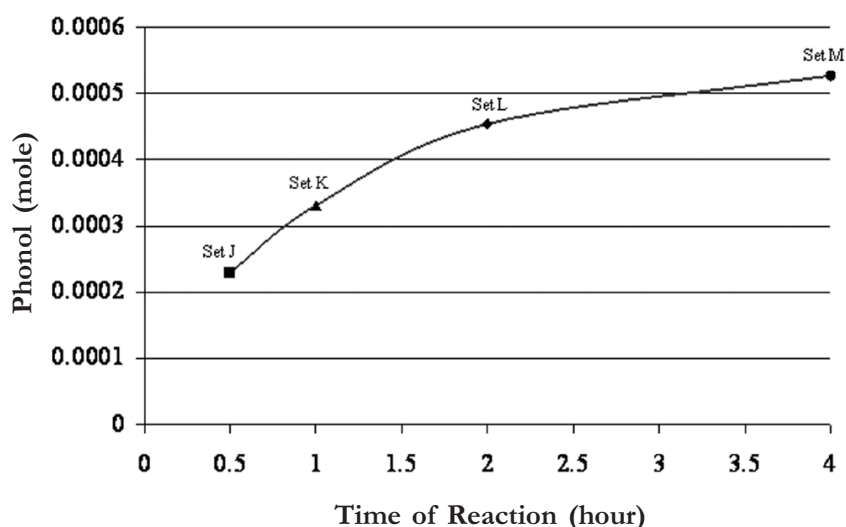


Figure 5. The effect of reaction time on the mole number of phenol produced.

3.3 Hydroxylation of toluene

The hydroxylation of toluene using the best condition obtained from the hydroxylation of benzene shows 100% selectivity based on cresol products that preferred to form p-cresol higher than o-cresol.

4. CONCLUSION

The hydroxylation of benzene with hydrogen peroxide as an oxidant over TS-1, carried out in a bubble reactor, shows that when the volume of benzene feeding in each period was increased while the feeding frequency constant, the conversion of benzene

decreased. The amount of phenol increased when the reaction mixture was left for a period of time up to 4 hours, suggesting the reaction of benzene remained dissolving in the liquid phase. The extension of the experiment on the hydroxylation of toluene using the best condition obtained from the hydroxylation of benzene shows that o-cresol and p-cresol are two main hydroxylation products of toluene.

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