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Effects of HCl and HNO₃ on the oxidation of toluene to benzaldehyde by H₂O₂ over TS-1 modified with Al in aqueous phase

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Abstract

This research studies effects of HCl and HNO₃ in aqueous solution on the oxidation reaction between toluene and hydrogen peroxide to benzaldehyde over titanium silicalite-1 catalyst modified with Al. The reaction was carried out at reaction temperature 120°C in a pressurized autoclave reactor. The research found that the addition of HCl and HNO₃ not only increases the concentration of toluene in the aqueous phase but also increases the formation of benzaldehyde as main product in the reaction.

Keywords: Benzaldehyde, Toluene, TS-1, Hydrogen peroxide

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1. Introduction

Benzaldehyde is used as synthetic flavoring material and as a chemical intermediate in the manufacture of perfumes, flavoring chemicals, dyes, pharmaceuticals etc. In addition, it is also used as a precursor for the production of other organic compounds such as the synthesis of mandelic acid [1].

Currently, benzaldehyde is mainly produced from the chlorination of toluene process. In this process, toluene must firstly react with chlorine under the activation by light to produce benzyl chloride and benzal chloride. Then, benzal chloride is further hydrolyzed with water to benzaldehyde and HCl. The drawbacks of the chlorination process are (i) the use of light to initiate the chlorination reaction, (ii) the process involves more than one reaction step, and (iii) the formation of unwanted byproducts occur during the chlorination process. Therefore, a new process having fewer reaction steps and produces only benzaldehyde as the main product is still required.

Titanium Silicalite-1 (TS-1) is a microporous solid material in which some Si^{4+} ions in the MFI structure is replaced with Ti^{4+} ions. One of our research [2] found that the catalytic activity of TS-1 can be modified by adding some metal ions, i.e. Fe, Al, Co and V, to the catalyst. The modified catalysts behave differently from TS-1 in term of catalytic activity and product selectivities when used in the hydroxylation of benzene to phenol reaction.

In another previous work of our research, we found that TS-1 modified with other metals can act as a catalyst in the reaction between alkyl aromatics and H_2O_2 [3]. Furthermore, it is reported that that addition of Al into TS-1 did not destroy the structure of TS-1 and the TS-1 modified with Al catalyst yielded benzaldehyde as the major product in the reaction between toluene and H_2O_2 . To produce benzaldehyde from toluene in only one reaction step is therefore

possible. This work also showed that increasing the reaction temperature further increased the conversion of toluene [4].

The reaction between H_2O_2 and aromatic hydrocarbons (i.e. benzene and alkyl benzenes) is usually carried out in the liquid phase. If water is used as media, the progress of the reaction is found to be limited by the solubility of aromatic hydrocarbons in the aqueous phase which contains H_2O_2 [2-4]. Further study of our research group found that adding acids into the aqueous solution can increase the saturated concentration of benzene and toluene in water, thus increase the conversion [5]. Previous works also showed that the solubility rate and saturated concentration of benzene and toluene in water affected the extend of reaction [5,6].

The purpose of the present work is to improve the productivity of benzaldehyde from the reaction between toluene and H_2O_2 . The reaction is carried out in the liquid phase in a pressurized autoclave reactor. Water is used as reaction media. The concentration of toluene in the aqueous phase is adjusted by adding HCl and HNO_3 .

2. Research methodology

2.1 The preparation of the Al-TS-1 catalyst

A hydrothermal method was used to prepare titanium silicalite-1 modified with aluminiumcation (Al-TS-1) catalyst. Firstly, the gel solution was prepared by mixing 0.82 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.297 g of $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$, 2.39 g of NaOH, 4.99 ml of H_2SO_4 (conc.), 7.88 g of Tetrapropylammonium bromide (TPABr), 52.54 g of NaCl and 268 ml of de-ionized water. After that the gel mixture was gradually added by a solution of sodium silicate (69.0 g of sodium silicate and 45 ml of de-ionized water) and stirred to control the pH within the range 9-11. Then, the gel mixture was centrifuged for 15 minutes to separate the formed gel from the supernatant liquid. The precipitated gel mixture was

milled for a total of 1 hour. In order to separate the supernatant solution, the gel was milled for 15 minutes, alternating with being centrifuged for 15 minutes. Secondly, the decant solution was prepared by adding 0.82 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.2970 g of $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$, 3.40 ml of H_2SO_4 (conc.), 7.53 g of TPABr, 26.27 g of NaCl and 164 ml of de-ionized water. The supernatant liquid was separated from the mixture by centrifugation for 20 minutes. In the stage of crystallization, the mixture of gel in supernatant liquid was filled in a glass tube and placed in an autoclave. The autoclave was pressurized up to 3 barg by nitrogen gas and was maintained at 180°C for 3 days. Afterwards, the obtained crystal products were washed with de-ionized. Then, the crystals were dried in an oven at 110°C for at least 24 hours and calcined at 550°C in an air stream for 7 hours using a heating rate of $8.60^\circ\text{C}/\text{min}$. Then, the obtained Al-TS-1 was boiled at 80°C in 5 M of HNO_3 solution for 3 hours. After that the crystals were removed from the acid by washing with de-ionized water and dried at 110°C over night. The dried crystals were calcined again in an air stream at 550°C for 7 hours. After calcination, the final product was obtained as white solid powder.

2.2 Characterization of Al-TS-1 catalyst

BET surface area was measured using Micromeritics ASAP 2020. Catalyst composition was determined by XRF technique. The analysis was carried out on Siemens SRS 3400. FT-IR spectrum was recorded on Thermo Nicolet model Impact 400. The crystal structures were determined using x-ray diffraction (XRD) technique using $\text{CuK}\alpha$ radiation with Ni filter. Scans were performed over the 2θ ranges from 6° to 30° with step size $0.04^\circ/\text{sec}$.

2.3 The solubility of toluene in acidic solutions which the toluene was covered the surface of the aqueous phase

The rate of solubility and equilibrium concentrations of toluene in HNO_3 solutions was measured at room temperature. In each experiment 160 ml of acidic aqueous solution (0.05M, 0.1M, or 0.15M of nitric acid solutions) was added into a 250 ml beaker. Afterwards, a 1/4 inch OD stainless steel tube was vertically placed in the beaker to act as a sampling well. Then a volume of toluene was added to completely cover all the top surface of the aqueous phase. At a specify intervals, the stirring was stopped and liquid sample was taken from the vertically placed tube. Then, the concentration of dissolve toluene in the taken aqueous solution was analyzed by a gas chromatograph (Shimadzu GC8A) equipped with FID and GP10% packed column.

2.4 Oxidation of toluene by H_2O_2

The oxidation of toluene by H_2O_2 was carried out under vigorous stirring in a stainless steel SS304 reactor. 1 g of Al-TS-1, 120 ml of water or acidic aqueous solution, and 1.1 ml of toluene were added into the reactor. The reactor system was then pressurized up to 2 bar.g by nitrogen gas and heated up at 90°C using an oil bath and remained at this temperature for 1 hour to remove all gas in the pore of the catalyst. The reaction system is shown in Figure 1. After that the reactor temperature was raised to 120°C , the reaction temperature. To start the reaction, 1.0 ml of 30%wt H_2O_2 aqueous solution was injected via an injection port using a syringe. The reaction was carried out for 2 hours. To stop the reaction, the oil bath was removed and replaced with an ice bath. The two phases (aqueous and organic) were homogenized by adding 50 ml of ethanol. The catalyst was separated from the homogenized liquid phase by centrifugation.

The reaction products were analyzed with a gas chromatograph (Shimadzu modelGC8A) equipped with a FID. The column temperature was programmed to increase from 80°C to 230°C with a heating rate of 5°C/min.

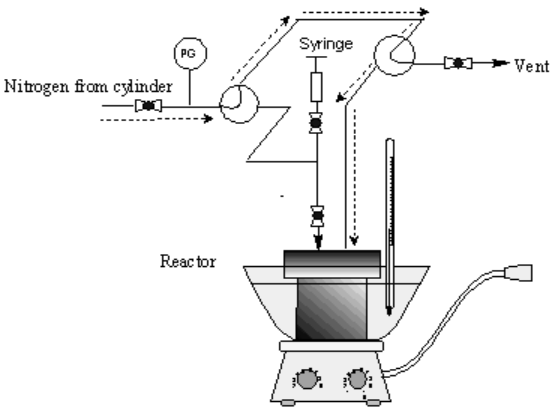


Figure 1 Schematic diagram of the reaction

3. Research results and discussion

3.1 Characterization of catalyst

Surface area of the catalyst was found to be 366.8 m²/g. The wt% of Ti and Al are 1.78 and 0.77, respectively. The x-ray diffraction (XRD) patterns shown in Figure 2 demonstrated only main typical peaks at 2θ = 8, 8.8, 14.8, 23.1, 24 and 26.7 which belong to MFI structure. The functional group analyzed using FT-IR (Figure 3) show the absorption band around 960 cm⁻¹. This confirms that Ti⁴⁺ had entered a silica lattice [7].

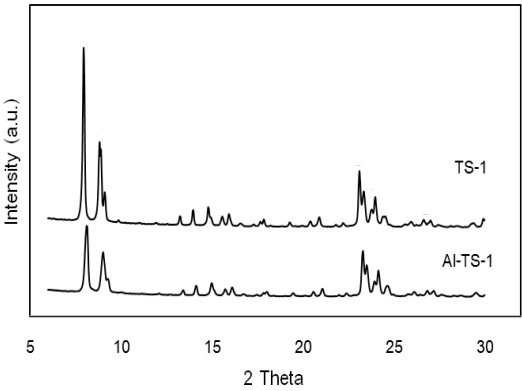


Figure 2 The XRD pattern of Al-TS-1.

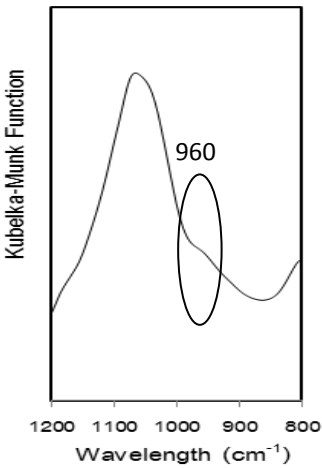


Figure 3 The FT-IR pattern of Al-TS-1.

Table 1 The effect of hydrochloric acid and nitric acid

Solution	Productivity (10 ⁻⁶ mol/gcat.min)		
	Benzaldehyde	<i>o</i> -Cresol	<i>p</i> -Cresol
HCl 0.1 M	12.63	0	6.64
HNO ₃ 0.1M	15.18	0	0
Deionized water	4.48	0.48	0.22

Table 2 The effect of different concentration of nitric acid

	Solution Concentration H_2O_2 conversion	
	(mol/L)	(%)
Nitric acid	0.05	34.74
	0.10	45.33
	0.15	18.31

3.2 Effects of HCl and HNO_3 on the oxidation of toluene to benzaldehyde over Al-TS-1 catalyst

The effect of acids on the reaction is compared using productivity of products. The definition of productivity is mole of product formed per weight of catalyst per reaction time. In our experiment the weight of catalyst is 1.0 g and the reaction time is 120 min. From the result in Table 1, one can see that the highest productivity of organic products (benzaldehyde plus cresols) was obtained in HCl solution. The higher productivity of benzaldehyde, however, is obtained when HNO_3 is used. In addition, in 0.1M HNO_3 solution, the reaction produces only one product, benzaldehyde. Therefore, the effect of concentration of nitric acid was the subject of further studied. The results obtained from using nitric acid solutions having different concentrations are reported in Table 2.

Since in this reaction, H_2O_2 is considered to be the irrecoverable reactant, the maximum consumption of H_2O_2 is important. The extent of the reaction is, therefore, reported in term of H_2O_2 conversion. The results in Table 2 show that there is an optimal concentration of nitric acid to yield the highest H_2O_2 conversion. This phenomenon can be explained from the solubility measurement results.

The solubility of toluene in the HNO_3 solution versus time is shown in Figure 4. The concentrations of HNO_3 solution were 0.05M, 0.10M and 0.15M. It was clear that the equilibrium concentration of toluene in 0.15M HNO_3 solution was the highest. The equilibrium concentration of toluene in different concentration of HNO_3 solutions could be arranged in the following order: 0.15M > 0.10M > 0.05M.

Due to the fact that the reaction occurs in the aqueous phase, initially the catalyst surface is rich with H_2O_2 molecule. Since the reaction follows the Langmuir-Hinshelwood model, if the concentration of toluene in the aqueous phase can be increased, the formation of benzaldehyde can be expected to increase. However, due to the nature of the catalyst surface which prefers non-polar molecules, too excessive toluene in aqueous will inhibit the adsorption of H_2O_2 on the catalyst surface. Hence, the conversion of H_2O_2 obviously decreases when excessive amount of nitric acid is used because it led to too high concentration of toluene in the aqueous phase. From each experiment benzaldehyde is found to be the only major product with a trace amount of cresols.

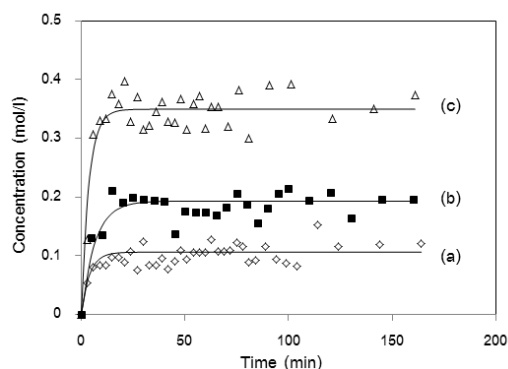


Figure 4 Solubility of toluene in different concentration of HNO_3 solutions, (a) 0.05M, (b) 0.10M, (c) 0.15M

4. Conclusion

This study has demonstrated that the addition of acid can increase the equilibrium concentration of toluene in the aqueous phase. Therefore, the conversion of H_2O_2 converted to benzaldehyde as main products in nitric acid solution can be enhanced.

5. References

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