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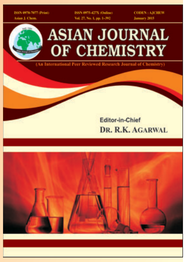

Low Temperature Catalytic Hydroxylation of Benzene to Phenol over SBA-15 as Supported Catalysts Under Microwave Irradiation

TONG LIU[1,*], JINHUI HOU[2] and YAOLI PENG[3]

[1]School of Chemistry & Chemical Engineering, Xuzhou Institute of Technology, Xuzhou 221111, Jiangsu Province, P.R. China
[2]School of Food (Biology) Engineering, Xuzhou Institute of Technology, Xuzhou 221111, Jiangsu Province, P.R. China
[3]School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221111, Jiangsu Province, P.R. China

*Corresponding author: E-mail: liutongcumt@126.com

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Liquid phase hydroxylation of benzene to phenol with hydrogen peroxide over catalysts prepared by the metallic compounds [*e.g.*, Fe(III), Cu(II), Co(II)] impregnated on SBA-15 was investigated at room temperature under microwave irradiation. This paper studied the catalytic performances of SBA-15 supports prepared by the various calcined temperature and time. The catalysts were characterized by N_2 adsorption technique. The Fe(III)/SBA-15 catalyst gave the highest conversion and yield than Cu(II), Co(II)/SBA-15 at same experimental condition. Various reaction parameters, such as amount of catalyst, amount of hydrogen peroxide and reaction time were investigated to obtain an optimal reaction conditions for phenol formation under microwave irradiation. Coupled conventionally heated method gives phenol yield of 8.9 %, the Fe(III)/SBA-15 gives higher phenol yield of 18.3 % and selectivity of 100 % under microwave irradiation conditions.

Keywords: Hydroxylation, Benzene, Phenol, SBA-15, Microwave irradiation.

INTRODUCTION

Phenol is an important chemical material in industry, which is the major source of phenol resins, fibers, adipic acid, aniline, salicylic acid and medicine[1,2]. Most of the worldwide production of phenol is based on the "cumene process," which has some disadvantages: high and damaging ecological impact, an explosive intermediate to manage (cumene hydroperoxide), large amount of acetone as by-product and a multistep character and restricts the industrial production of phenol[3-5]. Therefore, the study of the direct hydroxylation of benzene to phenol has attracted much attention in terms of an environment-friendly green process and economic efficiency[6,7].

In recent years, the direct hydroxylation of benzene with hydrogen peroxide as an oxidant has been widely explored in the mild conditions, because it is readily available and the producing by-products (molecular oxygen and water) are environmentally friendly[8,9]. Metal ion-exchanged or supported on hydrotalcites, zeolites and resins have been widely studied in order to overcome the disadvantage of homogeneous catalysts, recovery and reuse of the catalyst[10,11].

Compared to conventional heating method, microwave irradiation can remarkably accelerate a large-scale of chemical reactions under mild conditions, which is due to its many advantages, such as increasing energy efficiency, reducing the problems of low heat transfer and easy automation and incident power control[12]. Therefore, many chemical reactions that do not occur by conventional heating can proceed under microwave irradiation, especially in a polar system[13].

In present work, SBA-15 supports were prepared by the different calcined temperature and time to study the catalytic properties for hydroxylation of benzene to phenol at room temperature under microwave irradiation. Various metal (*e.g.*, Fe(III), Cu(II) and Co(II)) were loaded on SBA-15 support and catalytic performance of the obtained catalysts was compared. Finally, we have also studied the effect of various reaction parameters such as amount of catalyst used, amount of hydrogen peroxide used and reaction time on the yield of phenol.

EXPERIMENTAL

Catalyst preparation: The procedure for preparation of the SBA-15 materials was the following. Tetraethyl orthosilicate (TEOS) was used as the sources of Si. 4.06 g of pluronic P123 triblock copolymer surfactant ($EO_{20}PO_{70}EO_{20}$, Mav = 5800) and 0.68 g of polyethylene-glycol (PEG) were dissolved in 150 mL of distilled water and 10 mL of 2 M HCl was added dropwise to the solution as a catalyst. 22.78 mL of 0.1 M TEOS solution was added to above solution under continuous stirring for 6 h to make the solution homogeneous. The resulting mixture was stirred for 8 h at 45 °C and then aged at 80 °C for 15 h. The crystallized product was filtered, washed with deionized water, dried at room temperature for 24 h and finally calcined at various temperatures (*e.g*., 400, 500 and 600 °C) and times (*e.g*., 2, 4 and 6 h) under oxygen atmosphere (O_2 flow rate: 40 mL min^{-1}) to remove the template.

Catalysts metal oxides/SBA-15 were prepared by impregnated method was as follows: an aqueous solution which dissolved the prescribed amounts of metallic salt (*e.g*., $FeCl_3 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$) and SBA-15 is stirred for 4 h at room temperature. Then the solution containing precipitates was filtrated and the solid product obtained was further dried at 80 °C and overnight in vacuum oven. The dry catalysts were calcined at 500 °C and 4 h to remove the organic template. After calcination, the catalysts were stored in a dessicator.

Catalytic hydroxylation of benzene: The catalytic hydroxylation of benzene to phenol was carried out: 1 mL of benzene, 15 mL acetonitrile, 35 °C reaction temperature, described amounts of catalyst and H_2O_2 (30 %) were added into a 50 mL CEM discover microwave reactor with a magnetical stirrer. The reactor was kept for 5-30 min. Then the reactor was immediately cooled to room temperature by purging compressed air. The reaction mixtures were analyzed by GC/MS.

The BET surface area, total pore volume and pore size distribution of the fresh catalysts were determined *via* N_2 physisorption at the normal boiling point of N_2 (-196 °C), using an Autosorb-1MP instrument (Quanta chrome, USA).

Reaction performances are defined as follows:

$$\text{Yield of phenol} = \frac{\text{Mole of phenol produced}}{\text{Inintial mole of benzene}}$$

$$\text{Selectivity phenol} = \frac{\text{Mole of phenol produced}}{\text{Mole of benzene reacted}}$$

RESULTS AND DISCUSSION

Effect of prepared conditions of SBA-15 on the yield of phenol under microwave irradiation

Effect of calcined temperature: The results for the effect of calcined temperature (*e.g*., 400, 500 and 600 °C) and 4 h of SBA-15 used as Fe(III)/SBA-15 catalysts support on the yield of phenol under microwave irradiation is shown in Table-1. It is found that calcined temperature 500 °C of SBA-15 offers the highest conversion than 400 and 600 °C. This may be due to the crystal phase of SBA-15 was perfectly converted at calcined temperature 500 °C. Thus, 500 °C is chosen as a suitable calcined temperature.

TABLE-1
EFFECT OF CALCINED TEMPERATURE

Temperature (°C)	Conversion (%)	Selectivity (%)
400	10.1	100
500	18.3	100
600	13.7	100

Reaction conditions: 0.5 g catalyst, 1 mL benzene, 3mL H_2O_2, 20 mL acetonitrile, 35 °C, 25 min

Effect of calcined time: Effect of the calcined time (*e.g*., 2, 4 and 6 h) and 500 °C of SBA-15 used as Fe(III)/SBA-15 catalysts support on benzene conversion and phenol selectivity under microwave irradiation is summarized in Table-2. The results exhibited that the calcined time of 4 h offered highest activity than other calcined time, which may be due to the crystal phase of catalyst was perfectly not converted at 2 h and the further increasing calcined time to 6 h caused the crystal reunion. Therefore, 4 h is considered as a suitable calcined time.

TABLE-2
EFFECT OF CALCINED TIME

Time (h)	Conversion (%)	Selectivity (%)
2	11.2	100
4	18.3	100
6	13.2	97

Reaction conditions: 0.5 g catalyst, 1 mL benzene, 3 mL H_2O_2, 20 mL acetonitrile, 35 °C, 25 min

Effect of Fe(III) loading: Influence of the different loading amount (*e.g*., 3, 5 and 7 %) of Fe(III)/SBA-15 catalysts on the benzene conversion and phenol selectivity was investigated under microwave irradiation. As shown in Table-3, the conversion of benzene increases with the increasing of Fe(III) loading. However, the selectivity of phenol obviously reduced. That may be due to the increasing amount of metal active species causes the increasing in the hydroxyl free radical generation and thus to enhance the yield of phenol. However, the excessive metal species reduces of dispersion of the catalyst metal. Thus, an optimum yield of 5 % was observed.

TABLE-3
EFFECT OF DIFFERENT LOADED AMOUNT IN Fe(III)/SBA-15 CATALYSTS PREPARED BY THE IMPREGNATED METHOD ON CATALYTIC ACTIVITY

Fe(III)/SBA-15 (wt %)	Conversion (%)	Selectivity (%)
3	11.2	100
5	18.3	100
7	21.9	81

Reaction conditions: 0.5 g catalyst, 1 mL benzene, 3 mL H_2O_2, 20 mL acetonitrile, 35 °C, 25 min

Effects of metal species supported on SBA-15 on the yield of phenol under microwave irradiation: The metal species/SBA-15 catalysts were prepared by impregnated method from three precursors: Fe(III) trichloride, Cu(II) nitrate, Co(II) nitrate. The effect of different metal species supported on SBA-15 catalysts on benzene conversion and phenol selectivity under microwave irradiation are summarized in Table-4. It was noted that the activity of metal catalysts followed the order: Fe(III) > Cu(II) > Co(II). However, BET surface area and pore volume followed the opposite order (as shown in Table-5). The results indicate that the Fe(III) was located more amount on the surface of SBA-15 than other metal species. In addition, it is clear that the type of precursor influenced the metal distribution on the surface of catalysts.

Effect of reaction conditions on the yield of phenol under microwave irradiation

Effect of amount of catalyst: Influence of the amount of Fe(III)/SBA-15 (5 wt %) catalyst on the yield of phenol under microwave irradiation was studied. Table-6 showed that no phenol was detected without the use of Fe(III)/SBA-15 catalyst, indicating that the presence of Fe(III) is essential for performing the reducer. When the amount of catalyst increased from 0.1 to 0.5 g, the yield of phenol increased greatly from 7.4 to 18.3 %. However, a further increase in the amount of catalyst to 0.5 g caused a decrease in the yield of phenol. This may be due to the rapidly increasing in the hydroxyl free radical

TABLE-4
EFFECT OF DIFFERENT METAL SPECIES/SBA-15 CATALYSTS PREPARED BY THE IMPREGNATED METHOD ON CATALYTIC ACTIVITY

Catalyst (5 wt %)	Conversion (%)	Selectivity (%)
Fe(III)/SBA-15	18.3	100
Cu(II)/SBA-15	7.2	90
Co(II)/SBA-15	4.1	85

Reaction conditions: 0.5 g catalyst, 1 mL benzene, 3 mL H_2O_2, 20 mL acetonitrile, 35 °C, 25 min

TABLE-5
BET DATA FOR DIFFERENT METAL SPECIES/SBA-15 CATALYSTS PREPARED BY THE IMPREGNATED METHOD

Catalyst (5 wt %)	Surface area ($m^2 g^{-1}$)	Total pore volume ($mL g^{-1}$)	Average pore diameter (nm)
Fe(III)/SBA-15	712.4	1.12	4.12
Cu(II)/SBA-15	756.1	1.41	4.62
Co(II)/SBA-15	792.2	1.54	4.85

TABLE-6
EFFECT OF THE CATALYST AMOUNT ON CATALYTIC ACTIVITY UNDER MICROWAVE IRRADIATION

Fe(III)/SBA-15 (g)	Conversion (%)	Selectivity (%)
0	0	0
0.1	7.4	100
0.3	11.8	100
0.5	18.3	100
0.7	22.7	87

Reaction conditions: 1 mL benzene, 3 mL H_2O_2, 20 mL acetonitrile, 35 °C, 25 min

generation with the increase of catalyst amount and thus to improve the yield of phenol; but an excess of hydroxyl free radical generated inevitably promoted opposite effect occured, reduced the yield of phenol. So, 0.5 g is chosen as a suitable amount in this reaction.

Effect of amount of H_2O_2: Effect of the amount of H_2O_2 as the oxidant for the hydroxylation of benzene on the yield of phenol over Fe(III)/SBA-15 (5 wt %) catalysts at room temperature under microwave irradiation is shown in Table-7. It is found that no phenol was obtained without the use of H_2O_2. When the amount of H_2O_2 increased from 1 to 3 mL, the yield of phenol increased from 5.6 to 18.3 %. However, further increase of the amount of H_2O_2 caused the yield of phenol dropped quickly. It can be explained that further oxidation of phenol to hydroquinone or benzoquinone can be occurred with the presence of excessive amount of H_2O_2. Therefore, 3 mL is considered as a suitable amount in this reaction.

Effect of reaction time on the yield of phenol: Effect of reaction time on the yield of phenol over Fe(III)/SBA-15 (5 wt %) catalysts at room temperature under microwave irradiation is illustrated in Table-8. It can be observed that the reaction time increased from 5 min to 25 min, the yield increased sharply from 3.6 to 18.3 % and after that, the yield decreased sharply with the further increase of reaction time to 0.5 h. This maybe due to the further oxidation of the phenol. Thus, 25 min is chosen as a suitable reaction time in this reaction.

Conclusion

The liquid phase hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by transition metals supported on SBA-15 catalysts at room temperature under microwave irradiation was investigated. The optimum calcined condition for SBA-15 supported is 500 °C calcined temperature and 4 h calcined time. The activity of different metals salts supported on SBA-15 catalyst in production of phenol was Fe(III) > Cu(II) > Co(II). SBA-15 supported catalysts containing 3, 5, 7 w/t % Fe(III) was tested for their catalytic activity. It was found that 5 wt % gave the best phenol yield. The Fe(III)/SBA-15 (5 wt %) prepared under optional preparation conditons exhibits the high activity for the conversion of benzene with 18.3 and 100 % selectivity of phenol at the optimum reaction conditions: l mL benzene, 20 mL acetonitrile, 0.5 g catalyst, 3 mL 30 % aqueous solution of H_2O_2, 25 min reaction time, 35 °C reaction temperature.

TABLE-7
EFFECT OF THE H_2O_2 AMOUNT ON CATALYTIC ACTIVITY UNDER MICROWAVE IRRADIATION

H_2O_2 (mL)	Conversion (%)	Selectivity (%)
0	0	0
1	5.6	100
2	11.7	100
3	18.3	100
4	22.5	78

Reaction conditions: 0.5 g catalyst, 1 mL benzene, 20 mL acetonitrile, 35 °C, 25 min

TABLE-8
EFFECT OF THE REACTION TIME ON CATALYTIC ACTIVITY UNDER MICROWAVE IRRADIATION

Time (min)	Conversion (%)	Selectivity (%)
5	3.6	100
10	7.2	100
15	10.1	100
20	13.7	100
25	18.3	100
30	22.1	79

Reaction conditions: 0.5 g catalyst, 1 mL benzene, 3 mL H_2O_2, 20 mL acetonitrile, 35 °C

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REFERENCES

1. K. Lemke, H. Ehrich, U. Lohse, H. Berndt and K. Jähnisch, *Appl. Catal. A*, **243**, 41 (2003).
2. L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, R. Tassinari and R. Ungarelli, *Angew. Chem. Int. Ed.*, **115**, 5087 (2003).
3. I. Yuranov, D.A. Bulushev, A. Renken and L. Kiwi-Minsker, *Appl. Catal. A*, **319**, 128 (2007).
4. K.S. Pillai, J. Jia and W.M.H. Sachtler, *Appl. Catal. A*, **264**, 133 (2004).
5. J.K. Joseph, S. Singhal, S.L. Jain, R. Sivakumaran, B. Kumar and B. Sain, *Catal. Today*, **141**, 211 (2009).
6. A. Nemati Kharat, S. Moosavikia, B. Tamaddoni Jahromi and A. Badiei, *J. Mol. Catal. Chem.*, **348**, 14 (2011).
7. T. Liu, Y.X. Wang and J.H. Hou, *Asian J. Chem.*, **26**, 745 (2014).
8. T. Liu and J.H. Hou, *Asian J. Chem.*, **26**, 2683 (2014).
9. Y.Y. Gu, X.H. Zhao, G.R. Zhang, H.M. Ding and Y.K. Shan, *Appl. Catal. A*, **328**, 150 (2007).
10. X.K. Hu, L.F. Zhu, X.Q. Wang, B. Guo, J.Q. Xu, G.Y. Li and C.W. Hu, *J. Mol. Catal. Chem.*, **342-343**, 41 (2011).
11. R. Molinari and T. Poerio, *Appl. Catal. A*, **393**, 340 (2011).
12. C. Bonnet, L. Estel, A. Ledoux, B. Mazari and A. Louis, *Chem. Eng. Process.*, **43**, 1435 (2004).
13. P.A. Enquist, P. Nilsson and M. Larhed, *Org. Lett.*, **5**, 4875 (2003).