



Low Temperature Hydroxylation of Benzene to Phenol on Fe/Activated Carbon Catalysts Loaded with Different Types of Second Metal Under Microwave Condition

T. LIU^{1,*} and J.H. Hou²

¹School of Chemistry and Chemical Engineering, Xuzhou Institute of Technology, Xuzhou 221111, Jiangsu Province, P.R. China

²School of Food (Biology) Engineering, Xuzhou Institute of Technology, Xuzhou 221111, Jiangsu Province, P.R. China

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

Received: 21 October 2013;

Accepted: 12 December 2013;

Published online: 30 September 2014;

AJC-16099

This paper investigated the microwave assisted liquid phase hydroxylation of benzene to phenol with hydrogen peroxide over Fe/activated carbon-based catalysts prepared by impregnated method. Various types of second metal (*e.g.*, Co and Cu) were loaded together with Fe on the activated carbon support and the catalytic performance of the obtained catalysts was compared. It was found that the presence of the second metal can improve the phenol production of the typical Fe/activated carbon catalyst. Various techniques (XRD and BET surface area) were employed to characterize the catalysts. Finally the effects of some operating variables (*e.g.*, reaction time, catalyst amount, H₂O₂ amount, solvent amount) on the catalytic performance were investigated.

Keywords: Microwave, Hydroxylation, Benzene, Phenol, Hydrogen peroxide.

INTRODUCTION

Phenol is a valuable organic intermediates in chemical industries related to resin, pharmaceuticals, agrochemicals, nylon and other synthetic fibers¹⁻³. Nowadays, 90 % of the worldwide production of phenol is based on the cumene process, which constitutes a three-step reaction that has as main advantage the conversion of the two relatively inexpensive starting materials, benzene and propene, into the valuable chemicals phenol. However, the process suffers from many disadvantages such as the lower conversion and formation of acetone as inevitable side product⁴⁻⁷. Therefore, the one-step process for direct hydroxylation of benzene to phenol has attracted worldwide attention and is one of the most challenging issues in catalysis research at present^{8,9}.

The synthesis of phenol from the direct hydroxylation of benzene can be achieved by various oxidants, including nitrous oxide¹⁰, hydrogen peroxide¹¹ and molecular oxygen¹². Hydrogen peroxide has been widely used as a green oxidant, because it is readily available and the resulting by-products (water and molecular oxygen) are environmentally friendly^{13,14}.

Microwave irradiation is well documented to significantly accelerate a wide range of organic reactions, especially in a polar system, under mild conditions¹⁵. Microwave irradiation heating has the following advantages compared to conventional heating for organic reactions: no direct contact between the energy source and the reacting chemicals¹⁶, reducing heat

transfer problems¹⁷, energy efficiency¹⁸, easy automation and incident power control¹⁹. In numerous organic reactions, rapid heating, selective heating and enhancements of yield and purity are possible by microwave irradiation²⁰.

In this study, we attempted to improve the catalytic properties of the Fe/activated carbon catalyst by adding second metal oxides (Cu and Co) at different compositions to the catalysts for the liquid phase hydroxylation of benzene to phenol with hydrogen peroxide at room temperature. In addition, various techniques were employed to characterize the synthesized catalysts. Finally, the effects of some operating variables such as reaction time, catalyst amount, H₂O₂ amount, solvent amount on the phenol yield were investigated.

EXPERIMENTAL

Catalyst preparation: All solvents and reagents were purchased from commercial sources and used without further purification. Activated carbon was treated by refluxing with 5 M nitric acid for 3 h, then the material was washed until neutral pH was attained. By filtrating, the solid obtained was further dried at 70 °C overnight in vacuum. These activated carbons were then impregnated with a mixed solution of metal precursors at room temperature. For example, 5 wt. % Fe and 2.5 wt. % Cu loaded on activated carbon (abbreviated as Fe₅Cu_{2.5}/C) were prepared by mixing 10 g of activated carbon, 0.645 g of Fe (*e.g.*, 3.11 g of iron (III) chloride) and 0.21 g of Cu (*e.g.*,

0.77 g of cupric(II) nitrate). Then, excess solvent was done by the vacuum evaporation. The catalyst samples were further dried at 70 °C overnight in vacuum oven.

Benzene hydroxylation: Benzene hydroxylation reaction was carried out in a CEM discover microwave reactor. The reactor contents were thoroughly mixed with the help of a magnetic stirrer. Acetonitrile was used as solvent and H₂O₂ (30 wt. %) as an oxidant. In all the experimental runs, 15 mL acetonitrile and 1 mL benzene were used. The reactor was heated to 35 °C for 5 to 20 min. Then the reactor was immediately cooled to room temperature by purging compressed air. The products were analyzed by gas chromatography.

Characterization: X-ray diffraction (XRD) measurements were carried out with a D/max-RA X-ray diffractometer (Rigaku, Japan), CuK_α radiation at a scan rate of 3°/min. The tube voltage and current were 35 kV and 35 mA, respectively. The phases were identified by comparing the diffraction patterns to standard powder XRD cards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS).

The BET surface area, total pore volume and pore size distribution of the fresh catalysts were determined *via* N₂ physisorption at the normal boiling point of N₂ (-196 °C), using an Autosorb-1 MP instrument (Quanta chrome, USA).

The terms of reaction performance were defined as follows:

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

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

RESULTS AND DISCUSSION

Evaluation of performances of various catalysts: The formulae of catalysts with different percent metal loadings are abbreviated by using subscripts; for example, Fe₅Cu₅/activated carbon represents a catalyst with 5 wt. % Fe and 5 wt. % Cu loaded on activated carbon.

The XRD patterns of the catalysts and the blank activated carbon support were determined. However, no obvious peaks of Fe, Cu and Co metals were observed when compared with the pattern of the blank activated carbon, which could be due to the low metal loading or to the oxide being in the amorphous state (not shown).

The catalytic activities of several activated carbon support second transition metal oxide catalysts in the direct hydroxylation of benzene to phenol with hydrogen peroxide under microwave irradiation at room temperature were tested in this work. The results summarized in Table-1 that the multi metal oxide catalysts within the studied ranges of percent loading of Cu and Co were more active for the hydroxylation of benzene to phenol than the Fe/activated carbon although the increase of the percent loading of second metal decreased the BET surface area and pore volume particularly at high values of metal loading (Table-2).

The effect of different loading amount of second metal oxides supported on activated carbon as catalyst were investigated. Both the different metal loadings of Cu and Co in the

catalyst were at the same value for all catalysts. The different loading amount of metal oxides obviously influenced the yield of phenol. The increase of the Cu and Co loadings improved the benzene conversion. However, the phenol selectivity obviously reduced. The decrease of selectivity at high metal loading could be due to the reduction of dispersion of the catalyst metal. The optimum percent loading of Cu and Co which offered the highest phenol yield was 5 wt. % (Fe₅Cu₅/activated carbon) giving a phenol selectivity of more than 75 %. The improved yield of phenol by the increase of metal loading was mainly contributed by the increase in the conversion. It is noted that the amounts of metal oxides in the catalysts have the effect on decomposition of H₂O₂ to hydroxyl radical and consequently the reactions taking place in the system.

TABLE-1
EFFECT OF Cu, Co-Fe/ACTIVATED CARBON CATALYSTS
PREPARED BY IMPREGNATED METHOD ON CATALYTIC
ACTIVITY UNDER MICROWAVE IRRADIATION

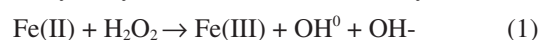
Catalyst	Conversion (%)	Selectivity (%)
5 wt. % Fe/C	28.9	100
2.5 wt. % Cu-5 wt. % Fe/C	31.4	89
5 wt. % Cu-5 wt. % Fe/C	37.3	75
2.5 wt. % Co-5 wt. % Fe/C	29.8	78
5 wt. % Co-5 wt. % Fe/C	32.2	71

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H₂O₂, 20 mL acetonitrile, 35 °C, 20 min

TABLE-2
BET DATA FOR Cu, Co-Fe/ACTIVATED CARBON
CATALYSTS PREPARED BY IMPREGNATED METHOD

Catalyst	Surface area (m ² g ⁻¹)	Total pore volume (mL g ⁻¹)	Average pore diameter (nm)
5 wt. % Fe/C	1107	1.04	3.76
2.5 wt. % Cu-5 wt. % Fe/C	1088	1.01	3.73
5 wt. % Cu-5 wt. % Fe/C	1071	1.00	3.70
2.5 wt. % Co-5 wt. % Fe/C	1098	1.02	3.75
5 wt. % Co-5 wt. % Fe/C	1091	1.01	3.73

Effect of the reaction conditions on the yield of phenol under microwave irradiation: Effect of the catalyst amount on the yield of phenol: The results for the effect of the amount of catalyst on the yield of phenol investigated over Fe₅Cu₅/activated carbon at room temperature under microwave irradiation is shown in Table-3. It was found that the catalyst amount increased from 0.2 to 0.3 g, the conversion of benzene increased slowly from 14.8 to 23.4 % and then sharply increased up to 37.7 % when the amount of catalyst was up to 0.4 g, but a further increase in the amount of catalyst inversely caused a decrease in the yield of phenol. The amount of catalyst has the effect on the decomposition of hydrogen peroxide and the amount of hydroxyl radical for this reaction system.

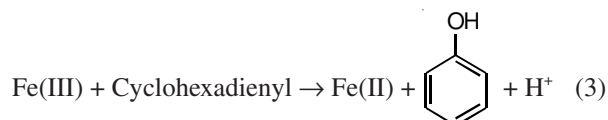
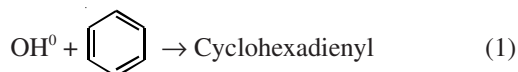


The increased amounts of catalyst increased the amount of hydroxyl radical in the reaction which is necessary for the oxidation reaction of benzene to produce cyclohexadienyl (CHD) radical as follows:

TABLE-3
EFFECT OF THE CATALYST AMOUNT ON REACTION
UNDER MICROWAVE IRRADIATION

Catalyst (g)	Conversion (%)	Selectivity (%)
0.2	14.8	89
0.3	23.4	85
0.4	37.7	81
0.5	39.7	74

Reaction conditions: 1 mL benzene, 3 mL H₂O₂, 20 mL acetonitrile, 35 °C, 20 min



Increasing the amount of catalyst increased the conversion of benzene but decreased phenol selectivity. The phenol was easy to produce byproducts (hydroquinone and benzoquinone), it is therefore essential to control the amount of hydroxyl radical per reactant. Therefore, 0.4 g Fe₅Cu₅/activated carbon is considered as a suitable amount in this reaction.

Effect of the amount of H₂O₂ for the hydroxylation of benzene: The effect of the amount of H₂O₂ for the hydroxylation of benzene on the yield of phenol over Fe₅Cu₅/activated carbon at room temperature under microwave irradiation is shown in Table-4. When the amount of H₂O₂ increased from 1 to 2 mL, the conversion of benzene increased slowly from 15.8 to 21.4 % and then sharply rose up to 37.7 % when the amount reached to 3 mL. However, when the amount of H₂O₂ was further up to 4 mL, 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 H₂O₂ oxidant. It was difficult to control the selective oxidation to produced phenol. The benzene conversion was increased by the high concentration of oxidant but it decreased the phenol selectivity. So, 3 mL is chosen as a suitable amount.

TABLE-4
EFFECT OF THE H₂O₂ AMOUNT ON REACTION
UNDER MICROWAVE IRRADIATION

H ₂ O ₂ (mL)	Conversion (%)	Selectivity (%)
1	15.8	88
2	21.4	84
3	37.7	81
4	39.9	72

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 20 mL acetonitrile, 35 °C, 20 min

Effect of the reaction time on the yield of phenol: The influence of reaction time on the yield of phenol over Fe₅Cu₅/activated carbon at room temperature under microwave irradiation is shown in Table-5. It is obvious that the conversion of benzene increased significantly from 13.8 to 37.7 % when the reaction time increased from 10 to 20 min and after that, the yield decreased sharply with the further increase of reaction time. The sharply decrease of yield may be caused by the further oxidation of the phenol. So, 20 min is chosen as a suitable reaction time in this reaction.

TABLE-5
EFFECT OF THE REACTION TIME ON REACTION
UNDER MICROWAVE IRRADIATION

Time (min)	Conversion (%)	Selectivity (%)
10	13.8	87
15	22.4	84
20	37.7	81
25	40.7	70

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H₂O₂, 20 mL acetonitrile, 35 °C

Effect of the amount of solvent on the yield of phenol:

The catalytic performance of the reaction system using different amounts of acetonitrile (*e.g.*, 10, 15, 20, 25, 30 mL) over Fe₅Cu₅/activated carbon at room temperature under microwave irradiation is summarized in Table-6. It should be noted that the benzene conversion significantly increased with increasing CH₃CN amount up to 20 mL but then decreased with further increase in CH₃CN amount. Strong interaction between benzene and OH[•] formed from H₂O₂ is necessary for the formation of phenol. Without CH₃CN, benzene and H₂O₂ aqueous solution are clearly divided into two layers. Reaction of benzene with OH[•] in the interface cannot proceed effectively. Since CH₃CN can be dissolved both in benzene and in aqueous solution of H₂O₂, adding proper amount of CH₃CN improves interaction between benzene and OH[•] formed from H₂O₂ and thereby increases phenol yield, but superfluous addition of CH₃CN decreases the concentrations of both benzene and H₂O₂ and subsequently decreases phenol yield instead. Therefore, 20 mL is chosen as a suitable solvent amount in this reaction.

TABLE-6
EFFECT OF THE SOLVENT AMOUNT ON REACTION
UNDER MICROWAVE IRRADIATION

Solvent Amount (mL)	Conversion (%)	Selectivity (%)
10	11.8	89
15	21.4	85
20	37.7	81
25	30.7	78
30	28.8	76

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H₂O₂, 35 °C, 20 min

Conclusion

The liquid phase hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by Fe/activated carbon with different values of metal loading under microwave irradiation was investigated. Fe₅Cu₅ catalyst was found to offer the highest yield. The second metal can improve the phenol production of the typical Fe/activated carbon catalyst. The highest yield of was achieved in the optimum condition under microwave irradiation: 1 mL benzene, 20 mL acetonitrile, 0.4 g catalyst, 3 mL 30 % aqueous solution of H₂O₂, 20 min reaction time, 35 °C reaction temperature.

ACKNOWLEDGEMENTS

The authors are grateful to the Scientific Research Item of Xuzhou Institute of Technology (grant No. XKY2012304) for the financial support.

REFERENCES

1. R. Klaewkla, T. Rirksomboon, S. Kulprathipanja, L. Nemeth and P. Rangsunvigit, *Catal. Commun.*, **7**, 260 (2006).
2. G.O. Rocha, R.A.W. Johnstone, B.F. Hemming, P.J.C. Pires and J.P. Sankey, *J. Mol. Catal. Chem.*, **186**, 127 (2002).
3. F. Xiao, J. Sun, X. Meng, R. Yu, H. Yuan, J. Xu and T. Song, *J. Catal.*, **199**, 273 (2001).
4. E. Hensen, Q. Zhu and R. Vansanten, *J. Catal.*, **233**, 136 (2005).
5. A.A. Ivanov, V.S. Chernyavsky, M.J. Gross, A.S. Kharitonov, A.K. Uriarte and G.I. Panov, *Appl. Catal. A.*, **249**, 327 (2003).
6. L.V. Pirutko, V.S. Chernyavsky, A.K. Uriarte and G.I. Panov, *Appl. Catal. A Gen.*, **227**, 143 (2002).
7. M. Tatlier and L. Kiwi-Minsker, *Catal. Commun.*, **6**, 731 (2005).
8. R. Dimitrova and M. Spassova, *Catal. Commun.*, **8**, 693 (2007).
9. Y.Y. Gu, X.H. Zhao, G.R. Zhang, H.M. Ding and Y.K. Shan, *Appl. Catal. A*, **328**, 150 (2007).
10. B. Liptakova, M. Hronec and Z. Cveňgrosova, *Catal. Today*, **61**, 143 (2000).
11. H. Liu, Z. Fu, D. Yin, D. Yin and H. Liao, *Catal. Commun.*, **6**, 638 (2005).
12. E. Battistel, R. Tassinari, M. Fornaroli and L. Bonoldi, *J. Mol. Catal. Chem.*, **202**, 107 (2003).
13. J. Peng, F. Shi, Y. Gu and Y. Deng, *Green Chem.*, **5**, 224 (2003).
14. P. Lidström, J. Tierney, B. Wathey and J. Westman, *Tetrahedron*, **57**, 9225 (2001).
15. S.A. Galema, *Chem. Soc. Rev.*, **26**, 233 (1997).
16. C. Gabriel, S. Gabriel, E.H. Grant, E.H. Grant, B.S.J. Halstead and D.M.P. Mingos, *Chem. Soc. Rev.*, **27**, 213 (1998).
17. B.D.M.P. Mingos and D.R. Baghurst, *Chem. Soc. Rev.*, **20**, 1 (1991).
18. P.A. Enquist, P. Nilsson and M. Larhed, *Org. Lett.*, **5**, 4875 (2003).
19. C. Bonnet, L. Estel, A. Ledoux, B. Mazari and A. Louis, *Chem. Eng. Process.*, **43**, 1435 (2004).
20. D.R. Baghurst and D.M.P. Mingos, *J. Chem. Soc. Chem. Commun.*, **9**, 674 (1992).