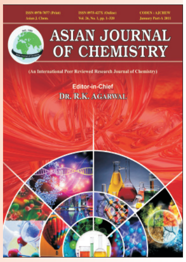
Asian Journal of Chemistry; Vol. 26, No. 11 (2014), 3209-3212

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.15884



Iron(III) Supported γ-Al_2O_3 Catalyst for Hydroxylation of Benzene

T. Liu[1,*] and J.H. Hou[2]

[1]School of Chemistry and 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

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

Received: 8 June 2013; *Accepted*: 16 August 2013; *Published online*: 25 May 2014; AJC-15214

The liquid-phase catalytic oxidation of benzene to directly produce phenol was studied under microwave irradiation using $FeCl_3$/γ-Al_2O_3 as the catalysts prepared by the microwave-impregnated method. The catalysts were characterized by XRD and N_2 adsorption techniques. The results indicated that the performance of the catalysts was significantly affected by the amount of Fe(III) loaded onto the γ-Al_2O_3 and microwave irradiation time. The influence of the reaction conditions, such as reaction temperature, the amount of catalyst, amount of hydrogen peroxide on the yield of phenol was investigated under microwave irradiation. Coupled conventionally heated method gives phenol yield of 9.8 %, the $FeCl_3$/γ-Al_2O_3 prepared by the microwave- impregnated method gives higher phenol yield of 15.2 % and selectivity of 100 % when irradiated with microwave energy.

Keywords: Benzene, Phenol, $FeCl_3$/γ-Al_2O_3, Microwave-impregnated, Hydrogen peroxide.

INTRODUCTION

Phenol is the most important intermediates for the manufacturing of petrochemicals, agrochemicals and polymers[1,2]. More than 90 % of the world production is obtained by the cumene process. However, this process has several disadvantages *e.g.*, low one-pass yield of phenol, high energy cost and the production of equal amount of acetone as the by product[3]. Therefore, the direct hydroxylation of benzene to phenol with high atom utilization and high selectivity has attracted much attention[4,5].

In recent years, this interesting work has been extensively studied in finding a suitable solid catalyst for the selective oxidation of benzene to phenol under mild reaction conditions with H_2O_2 as an oxidant[6-10]. The solvent is usually added to the reaction system for dissolving hydrogen peroxide and benzene into one phase for the oxidation of benzene to phenol. Several solvents such as acetone, acetonitrile, acetic acid, pyridine and dichloromethane have been employed. However, there are only a few works comparing the effect of solvent types[11,12].

In the present work, we prepared the $FeCl_3$/γ-Al_2O_3 by the microwave-impregnated method and indicated that the performance of the catalysts was significantly affected by the amount of Fe loaded onto the γ-Al_2O_3 and microwave irradiation time. We also explored the optimal reaction conditions for phenol formation under microwave irradiation, obtained phenol yield of 15.2 % and selectivity of 100 %.

EXPERIMENTAL

All the reagents, including benzene, γ-Al_2O_3 (200 mesh), $FeCl_3\cdot 6H_2O$, H_2O_2 (30 % by weight) and acetonitrile, were commercially purchased and used without further purification.

Catalyst preparation: The aqueous solution which dissolved the prescribed amounts of $FeCl_3\cdot 6H_2O$ and γ-Al_2O_3 along with a magnetical stirrer were placed into a 100 mL CEM discover microwave reactor. The reactor was heated to 80 °C and kept at that temperature for 5-30 min. Then the solution containing precipitates was filtrated and the solid product obtained was further dried at 70 °C overnight in vacuum oven.

Catalytic tests: A typical oxidation reaction is as follows: 1 mL of benzene, 15 mL of acetonitrile, described amounts of catalyst and H_2O_2 were added into a 50 mL CEM discover microwave reactor with a magnetical stirrer. The reactor was heated to an indicated temperature and kept at that temperature for 10-40 min. Then the reactor was immediately cooled to room temperature by purging compressed air. The reaction mixture was analyzed by gas chromatography.

Characterization: X-ray diffraction 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* N_2 physisorption at the normal boiling point of N_2 (-196 °C), using an Autosorb-1MP 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

Catalyst characterization: The XRD patterns of samples with the different loaded amount of $FeCl_3/\gamma\text{-}Al_2O_3$ catalysts prepared by the microwave-impregnated method was shown in Fig. 1. The broad diffraction peaks are observed over a range of 20° to 70°, which is in agreement with of $\gamma\text{-}Al_2O_3$ structure reported by the literature[13]. This indicates that the $\gamma\text{-}Al_2O_3$ structure was retained in the catalysts modified with promoters. In addition, no characteristic peaks of crystalline Fe_2O_3 phases were found in high-angle XRD patterns, suggesting that no bulk metal oxide was presented in all catalysts, which could be due to the low metal loading or to the oxide being in the amorphous state.

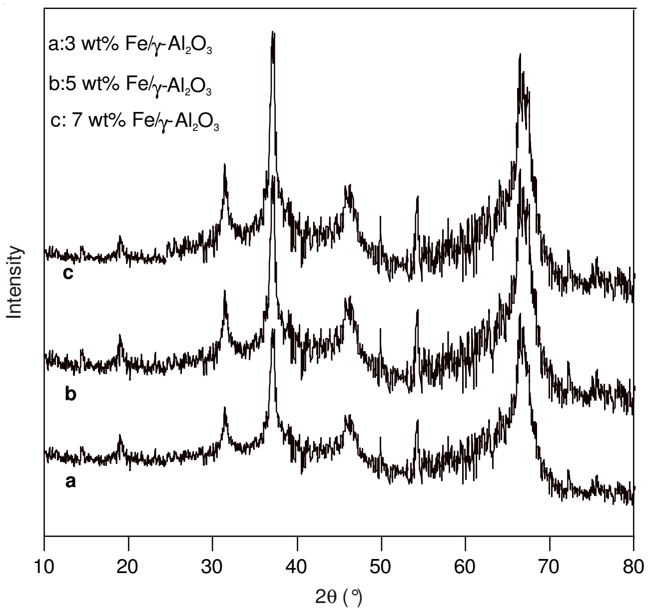


Fig. 1. XRD patterns of $FeCl_3/\gamma\text{-}Al_2O_3$ prepared by microwave impregnated method

Evaluation of performances of the catalysts preparation conditions by microwave impregnation method

Effects of transition metal species: The transition metal/ $\gamma\text{-}Al_2O_3$ catalysts were prepared from three precursors: Fe(III) trichloride, Cu(II) nitrate, Co(II) nitrate. The effects of the transition metal species on the benzene conversion, phenol selectivity and yields for different catalysts are summarized in Table-1. It was noted that the activity of transition 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-2). The results indicate that the Fe(III) was located more at the surface of $\gamma\text{-}Al_2O_3$ than other metal species. In addition, it is clear that the type of precursor influenced the metal distribution in the catalysts. As known, the catalytic activity of the transition metal species is dependent on the outer d electron density. Lesser the electron density, greater is the capacity of these transition metals to activate oxidant species like hydrogen peroxide. From the point of view of electron density the catalyst activity should be Fe(III) > Cu(II) > Co(II). So, Fe(III) is considered as a suitable precursor.

TABLE-1
EFFECT OF THE TRANSITION METAL SPECIES/$\gamma\text{-}Al_2O_3$ CATALYSTS PREPARED BY MICROWAVE IMPREGNATED METHOD ON CATALYTIC ACTIVITY

Catalyst (5 wt %)	Conversion (%)	Selectivity (%)
$FeCl_3/\gamma\text{-}Al_2O_3$	15.2	100
$Cu(NO_3)_2/\gamma\text{-}Al_2O_3$	5.2	100
$Co(NO_3)_2/\gamma\text{-}Al_2O_3$	4.5	95

Reaction conditions: 0.4 catalyst, 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 15 min

TABLE-2
BET DATA FOR THE TRANSITION METAL SPECIES/$\gamma\text{-}Al_2O_3$ PREPARED BY MICROWAVE IMPREGNATED METHOD

Catalyst (5 wt. %)	Surface area ($m^2 g^{-1}$)	Total pore volume ($mL g^{-1}$)	Average pore diameter (nm)
$FeCl_3/\gamma\text{-}Al_2O_3$	256.4	0.44	5.74
$Cu(NO_3)_2/\gamma\text{-}Al_2O_3$	281.1	0.51	6.48
$Co(NO_3)_2/\gamma\text{-}Al_2O_3$	292.3	0.56	6.58

Effect of the Fe(III) loading: The effect of the amount (*e.g.*, 3, 5, and 7 %) of Fe loaded onto the surface of the $FeCl_3/\gamma\text{-}Al_2O_3$ catalysts prepared by microwave impregnation method on the yield of phenol was shown in Table-3. The benzene conversion increased with increasing the amount of Fe loaded, while the selectivity decreased slightly. This situation because phenol can be further reacted to give catechol, benzoquinone and hydroquinone, which are undesirable by products. Thus, 5 % is considered as a suitable amount.

TABLE-3
EFFECT OF DIFFERENT LOADED AMOUNT IN $FECL_3/\gamma\text{-}Al_2O_3$ CATALYSTS PREPARED BY MICROWAVE IMPREGNATED METHOD ON CATALYTIC ACTIVITY

$FeCl_3/\gamma\text{-}Al_2O_3$ (wt. %)	Conversion (%)	Selectivity (%)
3	11.2	100
5	15.2	100
7	17.2	84

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 15 min

Effect of the microwave irradiation time: The results for the effect of the microwave irradiation time over 5 % (w/t) $FeCl_3/\gamma\text{-}Al_2O_3$ catalysts prepared by microwave- impregnation method on the yield of phenol was investigated at 80 °C are shown in Table-4. The phenol yield was found to increase with the increase of microwave irradiation time from 5 to 20 min.

However, further increased to 30 min, the yield of phenol decreased slightly. Thus, 20 min is considered as a suitable irradiation time.

TABLE-4
EFFECT OF THE MICROWAVE IMPREGNATED TIME ON CATALYTIC ACTIVITY

Time (min)	Conversion (%)	Selectivity (%)
5	7.8	100
10	11.2	100
20	15.2	100
30	14.0	100

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 15 min

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

Effect of the reaction time: The influence of reaction time on yield of phenol over 5 % (w/t) $FeCl_3$/γ-Al_2O_3 prepared by the microwave-impregnated method is shown in Fig. 2. It is obvious that the yield of phenol increase remarkably when the reaction time increased from 5 to 15 min and after that the yield decreased with further increase of reaction time. The decreased of yield may be caused by the further oxidation of the product. So, 15 min is chosen as a suitable reaction time.

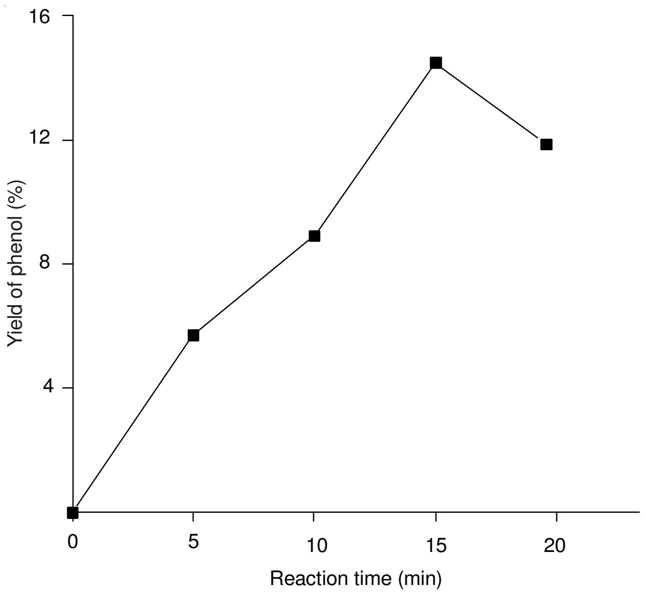


Fig. 2. Effect of reaction time on the yield of phenol, Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C

Effect of the amount of catalyst: As is indicated in Fig. 3, when the amount of catalyst increased from 0.1 to 0.4 g, the yield of phenol increased sharply from 6.2 to 15.2 %. On the other hand, a further increase in the amount of catalyst caused a decreased in the yield of phenol. This may be due to the oxidation of benzene by the use of catalyst. Therefore, 0.4 g, 5 % (w/t) $FeCl_3$/γ-Al_2O_3 is chosen as an optimum amount in this reaction.

Effect of the amount of H_2O_2: The effect of the amount of H_2O_2 on the yield of phenol is shown in Fig. 4. When the amount of H_2O_2 increased from 0.5 to 3 mL, the yield of phenol increased from 5.2 to 15.2 %. But a further increase in amount of H_2O_2 inversely caused a decrease in the yield of phenol. The yield of phenol had a maximum value at the amount of H_2O_2 around 3 mL.

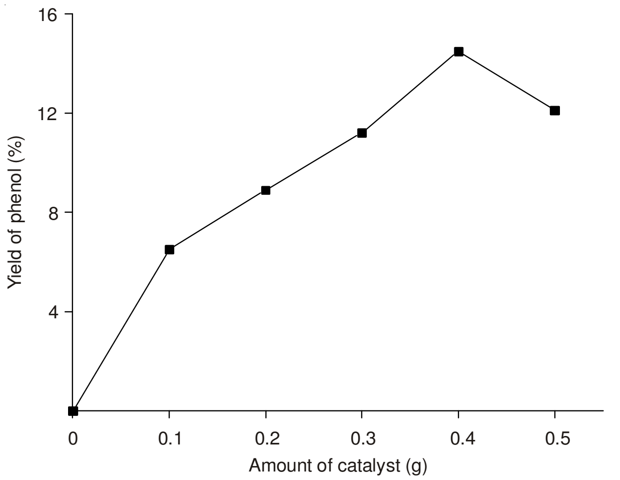


Fig. 3. Effect of catalyst amount on the yield of phenol, Reaction conditions: 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 15 min

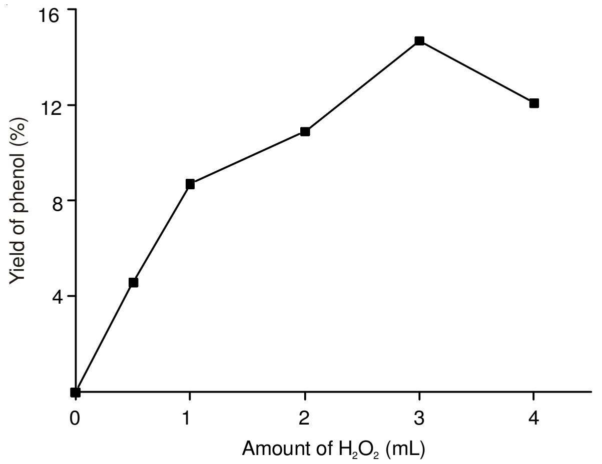
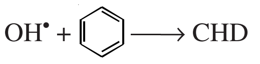


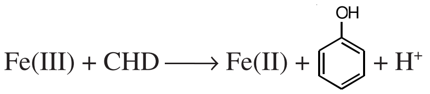
Fig. 4. Effect of H_2O_2 amount on the yield of phenol, Reaction conditions: 0.4 g catalyst, 1 mL benzene, 15 mL acetonitrile, 70 °C, 15 min

A classic Fenton-type system for benzene oxidation to phenol catalyzed by Fe(III)/γ-Al_2O_3 in the presence of H_2O_2 under microwave irridiation. The mechanism of Fenton system is widely accepted as follow:

$$\mathrm{Fe(II)} + H_2O_2 \longrightarrow \mathrm{Fe(III)} + OH^{\bullet} + OH^{-} \quad (1)$$



(2)



(3)

Both Fe(III) and Fe(II) play important roles in the reaction system. Fe(III) reacts with a cyclohexadienyl (CHD) radical intermediate to form phenol, while Fe(II) promotes the decomposition of hydrogen peroxide to a hydroxyl free radical. The amount of generated hydroxyl radicals which affects the phenol formation could be controlled by the amounts of H_2O_2 and metal catalyst added.

Conclusions

- The optional preparation conditons of $FeCl_3/\gamma\text{-}Al_2O_3$ by the microwave-impregnated method as follows: 0.5 % of loading amount and 15 min microwave irridiation time .
- The $FeCl_3/\gamma\text{-}Al_2O_3$ prepared under optional preparation conditons exhibits the high activity for the hydroxylation of benzene with 15.2 % phenol yield and 100 % selectivity of phenol at the optimum reaction conditions: 1 mL benzene, 15 mL acetonitrile, 0.4 g catalyst, 3 mL 30 % aqueous solution of H_2O_2, 15 min reaction time, 70 °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. T. Sakamoto, T. Takagaki, A. Sakakura, Y. Obora, S. Sakaguchi and Y. Ishii, *J. Mol. Catal.*, **288**, 19 (2008).
2. K. Lemke, H. Ehrich, U. Lohse, H. Berndt and K. Jähnisch, Appl. Catal. A, **243**, 41 (2003).
3. B. Lücke, K.V. Narayana, A. Martin and K. Jähnisch, *Adv. Synth. Catal.*, **346**, 1407 (2004).
4. H. Ehrich, H. Berndt, M.M. Pohl, K. Jähnisch and M. Baerns, *Appl. Catal. A*, **230**, 271 (2002).
5. A. Nemati Kharat, S. Moosavikia, B. Tamaddoni Jahromi and A. Badiei, *J. Mol. Catal.*, **348**, 14 (2011).
6. X.K. Hu, L.F. Zhu, X.Q. Wang, B. Guo, J.Q. Xu, G.Y. Li and C.W. Hu, *J. Mol. Catal.*, **342**, 41 (2011).
7. J. Zhang, Y. Tang, G. Li and C.W. Hu, *Appl. Catal. A*, **278**, 251 (2005).
8. M. Tani, T. Sakamoto, S. Mita, S. Sakaguchi and Y. Ishii, *Angew. Chem. Int. Ed.*, **44**, 2586 (2005).
9. S. Tamagaki, K. Hotta and W. Tagaki, *Chem. Lett.*, **11**, 651 (1982).
10. L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, R. Tassinari and R. Ungarelli, *Angew. Chem. Int. Ed.*, **42**, 4937 (2003).
11. Y. Zhong, G. Li, L. Zhu, Y. Yan, G. Wu and C. Hu, *J. Mol. Catal.*, **272**, 169 (2007).
12. J.S. Choi, T.H. Kim, K.Y. Choo, J.S. Sung, M.B. Saidutta, S.O. Ryu, S.D. Song, B. Ramachandra and Y.W. Rhee, *Appl. Catal. A*, **290**, 1 (2005).
13. Y.X. Li, T.S. Liu and J.F. Gao, *J. North. Chin. Inst. Technol.*, **25**, 277 (2004).