



Direct Hydroxylation of Benzene to Phenol Over Pyridine-Modified Vanadium-Substituted Heteropoly Acid Under Microwave Condition

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Direct oxidation of benzene to phenol over $\text{Py}_3\text{PMo}_{11}\text{V}$ and hydrogen peroxide as the oxidant under microwave irradiation. Pyridine(Py)-modified vanadium substituted heteropoly acid ($\text{Py}_3\text{PMo}_{11}\text{V}$) with Keggin structure was prepared and characterized by FT-IR. The influence of different reaction conditions, such as the reaction time, the amount of catalyst used, the amount of hydrogen peroxide used and the reaction temperature on the yield of phenol was studied to obtain the optimal reaction conditions for phenol formation. Coupled conventionally heated method gives phenol yield of 7.8 %, higher phenol yield of 24.7 % and selectivity of 100 % are obtained when irradiated with microwave energy.

Keywords: Oxidation of benzene, Phenol, Hydrogen peroxide, Microwave irradiation, Pyridine.

INTRODUCTION

Phenol is one of the most important intermediates of chemical industry¹. It is mainly produced by cumene process. However, this process suffers mainly from low atom utilization, low phenol yield, high energy consumption and the production of equal amount of acetone as the by product². Therefore, the study of the direct hydroxylation of benzene to phenol has attracted increasing interests for last decades³⁻⁵.

In recent years, there has been an increasing interest in Keggin-type heteropoly acids as catalysts for the hydroxylation of benzene to phenol, in which the substituted vanadium is known as the most active metal species^{6,7}. Moreover, because the strong acidity and redox property of Keggin-type heteropoly acids can be controlled by replacing the protons with metal cations and/or by changing the heteroatom or the framework transition-metal atoms, therefore, they have been studied for various reactions⁸⁻¹².

Microwave irradiation (MWI) as an energy source for many chemical reactions has been studied in recent years¹³. These studies show that it is well documented to significantly accelerate a wide range of chemical reactions, especially in a polar system, under mild conditions¹⁴.

In the present work, $\text{Py}_3\text{PMo}_{11}\text{V}$ was used as catalyst for the liquid-phase hydroxylation of benzene with 30 % H_2O_2 as an oxidant and observe the influence of microwave irradiation on catalytic reaction. The microwave provides more parameters

for convenient adjustment of reaction conditions. An obvious promotion effect of the catalyst on the phenol yield and selectivity was observed for this reaction.

EXPERIMENTAL

Catalyst preparation: All the reagents, including benzene, MoO_3 , pyridine, V_2O_5 , H_3PO_4 (85 %), H_2O_2 (30 % by weight) and acetonitrile, were commercially purchased and used without further purification.

The detailed procedure for the catalyst $\text{Py}_3\text{PMo}_{11}\text{V}$ preparation was as follows¹¹: 14.4 g MoO_3 and 0.92 g V_2O_5 were suspended in 250 mL deionized water in a 500 mL three-necked flask equipped with a condenser under magnetic stirring in an oil bath at the reflux temperature. 1.15 g aqueous 85 % H_3PO_4 was added drop-wise to the boiling and stirred suspension of the reaction mixture, a clear orange-red solution was obtained. The solution was cooled to the room temperature and further dried *via* evaporation to get a solid product, into which a suitable amount of deionized water was added to obtain a solution and then the solution was left at the room temperature overnight to re-crystallize for purification. The resulting fine orange-red powders was $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$. The catalyst $\text{Py}_3\text{PMo}_{11}\text{V}$ was prepared by the pyridine/ $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ molar ratio of 3:1. Then the solution containing precipitates was evaporated to dryness at 70 °C and the solid product obtained was further dried at the same temperature overnight in vacuum oven.

General procedure: The liquid-phase hydroxylation of benzene was carried out: 4 mL of benzene, 15 mL acetonitrile, described amounts of $\text{Py}_3\text{PMo}_{11}\text{V}$ and H_2O_2 (30 %) along with a magnetical stirrer were added into a 50 mL microwave reactor. The reactor was heated to an indicated temperature and kept at that temperature for 5–35 min. Then the reactor was immediately cooled to room temperature by purging compressed air. The reaction mixture was analyzed by gas chromatography.

The IR spectra of $\text{Py}_3\text{PMo}_{11}\text{V}$ was measured using a KBr disk mounted in an infrared spectrophotometer (ALPHA). Sample was mixed and grounded with KBr for IR measurement.

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 IR spectra of $\text{Py}_3\text{PMo}_{11}\text{V}$ is given in Fig. 1. The four IR vibration peaks assigned to a Keggin-type heteropoly acid can be seen from Fig. 1 and the locations of featured peaks (PsO, 1060 cm^{-1} ; MosOsMo, 966 cm^{-1} ; ModO, 863 and 779 cm^{-1}) are in well agreement with those in the previous report¹¹. After the reaction of pyridine with $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, the corresponding two peaks (1435 and 1381 cm^{-1}) of pyridine shifts to 1530 and 1484 cm^{-1} , respectively.

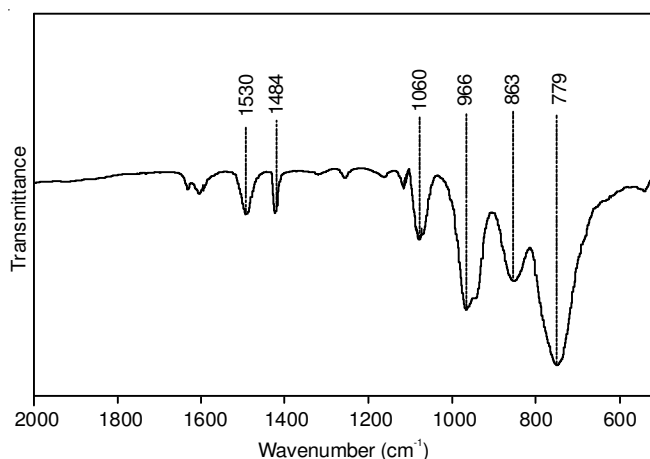


Fig. 1. FTIR spectra of $\text{Py}_3\text{PMo}_{11}\text{V}$ catalyst

Effect of the reaction temperature on the yield of phenol under microwave irradiation: The effect of the reaction temperature on the yield of phenol over $\text{Py}_3\text{PMo}_{11}\text{V}$ under microwave irradiation is shown in Fig. 2. It was indicated that the reaction temperature increased from 40 to 50 °C. The yield of phenol increased slowly from 11.4 to 13.5 %, showing a very slow reaction. When the reaction temperature was raised to 70 °C, a sharp increase to 24.7 % yield of phenol was obtained. However, when the reaction temperature was further up to 80 °C, caused the remarkable decrease of phenol yield

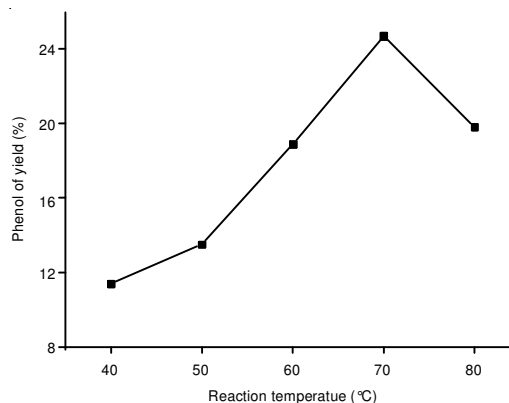


Fig. 2. Effect of reaction temperature on the yield of phenol. Reaction conditions: 0.15 g catalyst, 1 mL benzene, 1.8 mL H_2O_2 , 15 mL acetonitrile, time 20 min

to 19.7 %. This is mostly caused by decomposition of H_2O_2 proceeded faster at high temperature, leading to the excessive oxidation of the phenol and the lower value of the phenol yield. The above data indicate that the reaction temperature was increased to 70 °C promotes the production of phenol and self-decomposition of hydrogen peroxide. We have confirmed this trend by repeatedly carrying out this test. So, 70 °C is considered as a suitable hydroxylation reaction temperature.

Effect of the amount of H_2O_2 on the yield of phenol under microwave irradiation: The influence of H_2O_2 as the oxidant reagent on the yield of phenol was investigated using $\text{Py}_3\text{PMo}_{11}\text{V}$ as the catalyst and the effect of the amount of H_2O_2 on the yield of phenol is illustrated in Fig. 3. No phenol was obtained without the use of H_2O_2 . The phenol yield was found to increase with the increase of the amount of H_2O_2 and reached a maximum value of 24.7 % at 1.8 mL. Further increase of the amount of H_2O_2 had a reverse influence on the phenol yield, which result from the further oxidation of the phenol formed, the benzoquinone was observed. Therefore, 1.8 mL is considered as a suitable amount in this reaction.

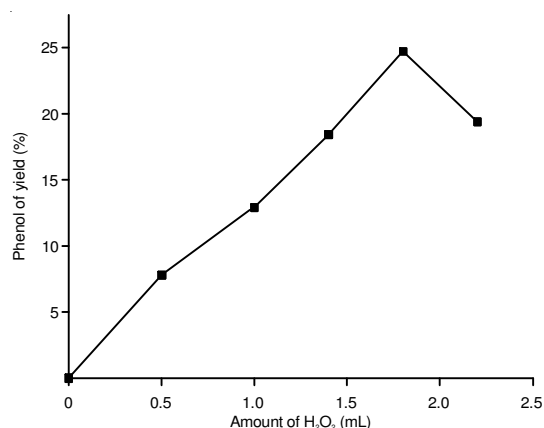


Fig. 3. Effect of H_2O_2 amount on the yield of phenol. Reaction conditions: 0.15 g catalyst, 1 mL benzene, 15 mL acetonitrile, 70 °C, time 20 min

Effect of the amount of catalyst on the yield of phenol under microwave irradiation: The effect of the amount of the $\text{Py}_3\text{PMo}_{11}\text{V}$ on the yield of phenol was investigated at 70 °C

and the results is shown in Fig. 4. No phenol was detected without the use of the $\text{Py}_3\text{PMo}_{11}\text{V}$, which indicated that $\text{Py}_3\text{PMo}_{11}\text{V}$ is essential for performing the reducer. The yield of phenol was increased from 0 to 24.7 % with the increase amount of the $\text{Py}_3\text{PMo}_{11}\text{V}$. When amount of the $\text{Py}_3\text{PMo}_{11}\text{V}$ is 0.15 g, the yield of phenol reached 24.7 % with a selectivity of 100 %. But further increase in the amount of the $\text{Py}_3\text{PMo}_{11}\text{V}$ inversely caused a decrease in the yield of phenol. Therefore, 0.15 g $\text{Py}_3\text{PMo}_{11}\text{V}$ is considered as a suitable amount in this reaction.

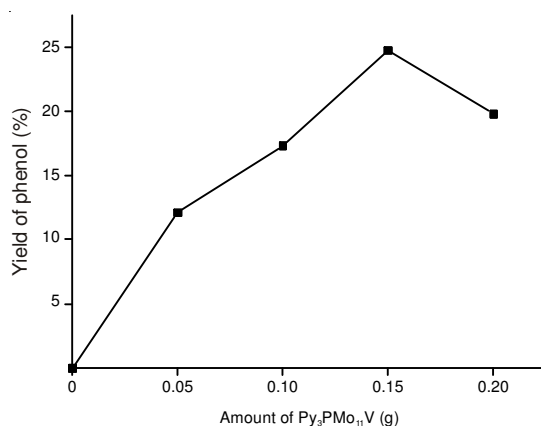


Fig. 4. Effect of catalyst amount on the yield of phenol. Reaction conditions: 1 mL benzene, 1.8 mL H_2O_2 , 15 mL acetonitrile, 70 °C, time 20 min

Effect of the reaction time on the yield of phenol under microwave irradiation: The influence of reaction time on the yield of phenol over $\text{Py}_3\text{PMo}_{11}\text{V}$ is shown in Fig. 5. It can be observed that the yield of phenol was a sharply increased to 24.7 % with the increased of reaction time up to 20 min. However, the yield decreased with the further increase of reaction time, which is due to the further oxidation of phenol. So 20 min is chosen as a suitable reaction time in this work.

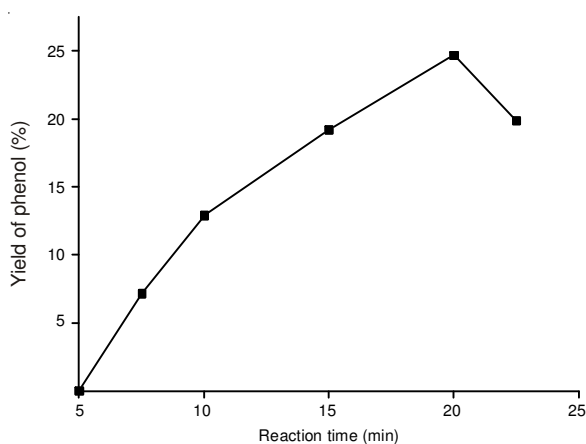


Fig. 5. Effect of reaction time on the yield of phenol. Reaction conditions: 0.15 g catalyst, 1 mL benzene, 1.8 mL H_2O_2 , 15 mL acetonitrile, 70 °C

Conclusion

Coupled conventionally heated method gives phenol yield of 7.8 %, $\text{Py}_3\text{PMo}_{11}\text{V}$ exhibits higher activity for the hydroxylation of benzene with 100 % selectivity of phenol and 24.7 % phenol yield under microwave irradiation at the optimum reaction conditions: 1.0 mL benzene, 0.15 g catalyst, 1.8 mL 30 % aqueous solution of H_2O_2 , 15 mL acetonitrile, 70 °C reaction temperature and 20 min reaction time.

Analysis the results, concluded that the substituted vanadium atom with high dielectric loss factor in heteropoly acid, can couple easily with microwave energy and gets heated, is essentially active site with higher performance for the hydroxylation of benzene to phenol under microwave irradiation.

REFERENCES

1. T. Sakamoto, T. Takagaki, A. Sakakura, Y. Obora, S. Sakaguchi and Y. Ishii, *J. Mol. Catal. A*, **288**, 19 (2008).
2. Y.-Y. Gu, X.-H. Zhao, G.-R. Zhang, H.-M. Ding and Y.-K. Shan, *Appl. Catal. A*, **328**, 150 (2007).
3. M. Tani, T. Sakamoto, S. Mita, S. Sakaguchi and Y. Ishii, *Angew. Chem. Int. Ed.*, **44**, 2586 (2005).
4. E. Battistel, R. Tassinari, M. Fornaroli and L. Bonoldi, *J. Mol. Catal. A*, **202**, 107 (2003).
5. 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).
6. K. Takahashi, T. Okuhara and M. Misono, *Chem. Lett.*, 841 (1985).
7. M. Misono, T. Okuhara, T. Ichiki and Y. Kanda, *J. Am. Chem. Soc.*, **109**, 5535 (1987).
8. B. Xu, Y. Wei, C.L. Barnes and Z. Peng, *Angew. Chem. Int. Ed.*, **40**, 2290 (2001).
9. Y.Y. Liu, K. Murata and M. Inaba, *Catal. Commun.*, **6**, 679 (2005).
10. B.B. Bardin and R.J. Davis, *Appl. Catal. A*, **185**, 283 (1999).
11. H.Q. Ge, Y. Leng, F.M. Zang, C.J. Zhou and J. Wang, *Catal. Lett.*, **124**, 250 (2008).
12. F.M. Zhang, J. Wang, C.S. Yuan and X.Q. Ren, *Catal. Lett.*, **102**, 171 (2005).
13. G. Bond, R.B. Moyes and D.A. Whan, *Catal. Today*, **17**, 427 (1993).
14. P. Lidström, J. Tierney, B. Wathey and J. Westman, *Tetrahedron*, **57**, 9225 (2001).