



Microwave-Assisted Hydroxylation of Benzene to Phenol Over V(V)/MCM-41 Catalysts at Room Temperature

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Direct hydroxylation of benzene to phenol with hydrogen peroxide over catalysts prepared by the metal species *e.g.*, V(V), Cu(II), Co(II) impregnated on MCM-41 was examined at room temperature under microwave irradiation. This paper investigated the catalytic performances of MCM-41 supports prepared by various calcined temperature and time. The results manifested that the V(V)/MCM-41 catalyst gave the highest activity than Cu(II), Co(II)/MCM-41 at same experimental conditions. The influence of various reaction parameters, such as reaction time, amount of catalyst and hydrogen peroxide, on the conversion of benzene was investigated under microwave irradiation. Coupled conventionally heated method gives phenol yield of 5.8 %, the V(V)/MCM-41 gives higher phenol yield of 18.7 % and selectivity of 100 % under microwave irradiation.

Keywords: Hydroxylation, Benzene, Phenol, Hydrogen peroxide, V(V)/MCM-41

INTRODUCTION

Phenol is an important intermediate for synthesis of various industrial products like phenol resins, epoxy resins, aniline, polycarbonates, caprolactam or bisphenol A^{1,2}. More than 90 % of the world's phenol production is based on the cumene route consisting of three main reaction steps. However, this route has several disadvantages *e.g.*, high energy cost, low one-pass yield of phenol and the production of equal amount of acetone as the by product^{3,4}. Therefore, the direct hydroxylation of benzene to phenol has attracted much attention for an environment-friendly green process and economic efficiency.

In recent years, many papers and monographs were published about the direct oxidation of benzene to phenol with various oxidants, including nitrous oxide, hydrogen peroxide or molecular oxygen⁵⁻⁷. Hydrogen peroxide as oxidant is widely attempted as a green oxidant at the mild conditions, which be due to its readily available and the resulting by-products (water and molecular oxygen) are environmentally friendly^{8,9}. Chemical compounds of vanadium, due to possess highly feasible reactivity and remarkable stability, have been widely used as the catalysts for a variety of oxidation reactions. Some researchers have reported about the benzene to phenol reaction over vanadium containing catalysts, such as VO_x species anchored on SBA-15 and clay, vanadium substituted polyoxo-metalates and phosphomolybdates^{10,11}.

Compared to conventional heating, microwave irradiation as an energy source for many chemical reactions has the following advantages, such as reducing heat transfer problems, energy efficiency, easy automation and incident power control^{12,13}. Therefore, many reactions that do not occur by conventional heating can proceed under microwave irradiation, especially in a polar system.

In this paper, MCM-41 supports were prepared by the different calcined temperature and time to examine the catalytic properties for hydroxylation of benzene to phenol with hydrogen peroxide as oxidant at room temperature under microwave irradiation. The effect of the different metal species like V(V), Cu(II) and Co(II) on phenol yield was investigated. The influence of various reaction parameters on the yield of phenol also has been studied. In addition, BET was employed to characterize the prepared catalysts. Finally, we have also explored the effect of various reaction parameters such as the reaction time, the amount of hydrogen peroxide and the amount of catalyst used on the yield of phenol.

EXPERIMENTAL

All the reagents, including benzene, NH₄VO₃, Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O, H₂O₂ (30 % by weight) and acetonitrile, were commercially purchased and used without further purification.

Preparation of MCM-41: Tetraethyl orthosilicate (TEOS) was used as Si source and cetyltrimethylammonium bromide (CTABr) was used as template. 0.6 g of NaOH was dissolved in 25 mL of water, 1.8 g of TEOS was added to the above solution under vigorously stirring for 2 h. And then, 1.9 g of CTABr was dissolved in 20 mL of water was added to the mixed solution with continuous stirring for 1 h more. The mixture was moved into a Teflon-lined stainless steel autoclave to make crystallization at 110 °C for 24 h. The product was filtered, washed with distilled water, dried at 80 °C for 10 h and calcined in air at various temperatures (*e.g.*, 450, 550, 650 °C) and times (*e.g.*, 3, 5, 7 h) to obtain MCM-41.

Catalysts metal oxides/MCM-41 were prepared according to the method described by Liu *et al.*⁹. A typical procedure was as follow: an aqueous solution which dissolved the prescribed amounts of metallic salt (*e.g.*, NH_4VO_3 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and MCM-41 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 550 °C and 5 h to remove the organic template. After calcination, the catalysts were stored in a dessicator.

Liquid-phase hydroxylation of benzene: A typical oxidation reaction is as follows: 1 mL of benzene, 25 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 10-30 min. Then the reactor was immediately cooled to room temperature by purging compressed air. The reaction mixtures were analyzed by GC/MS. The conversion of each substrate was calculated as molar ratio of the substrate remained in the reaction mixture to that added and the selectivity of each product was calculated as molar ratio of the product to all the products.

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-IMP 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

Effect of prepared conditions of MCM-41 on the yield of phenol

Effect of calcined temperature: The influence of the different calcined temperature (*e.g.*, 450, 550, 650 °C) and 5 h of MCM-41 used as V(V)/MCM-41 catalyst support on the yield of phenol at room temperature under microwave irradiation was studied. As shown in Table-1, the calcined temperature 550 °C of MCM-41 offers the highest conversion than 450 and 650 °C at same experimental conditions, which

TABLE-1
EFFECT OF CALCINED TEMPERATURE

Temperature (°C)	Conversion (%)	Selectivity (%)
450	11.1	100
550	18.7	100
650	14.1	100

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

may be due to the crystal phase of MCM-41 was perfectly converted at calcined temperature 550 °C. In addition, a further increasing calcined temperature to 650 °C, the crystal of MCM-41 may occur the sintering. So, 550 °C is chosen as a suitable calcined temperature.

Effect of calcined time: The results for the effect of the different calcined time (*e.g.*, 3, 5, 7 h) and 550 °C of MCM-41 used as V(V)/MCM-41 catalysts support on the yield of phenol at room temperature under microwave irradiation are summarized in Table-2. It is found that the calcined time of 5 h offered highest activity than other calcined times at same experimental conditions. This may be due to the crystal phase of MCM-41 was not perfectly converted in a short time, on the other hand, the further increasing calcined time to 7 h caused the crystal reunion. Thus, 5 h is considered as a suitable calcined time.

TABLE-2
EFFECT OF CALCINED TIME

Time (h)	Conversion (%)	Selectivity (%)
3	12.2	100
5	18.7	100
7	14.2	96

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

Effect of V(V) loading: The effect of the different loading amount (*e.g.*, 3, 5 and 7 %) of V(V)/MCM-41 catalysts on the benzene conversion and phenol selectivity at room temperature under microwave irradiation was shown in Table-3. The reaction test indicated that the increasing amount of the V(V) loadings from 3 to 7 % improved the benzene conversion; however, the phenol selectivity obviously reduced. That may be due to the increasing amount of V(V) causes the increasing in the hydroxyl free radical generation and thus to enhance the yield of phenol. However, an excess of hydroxyl free radical generated inevitably led to phenol secondary reaction occurred, reduced the yield of phenol. The specific surface area of the catalysts decreased with increased amount of V(V) loading (Table-4), indicating that some micropore blockage by V(V) species deposition on pore mouth. Therefore, 5 % was selected as an optimum V(V) loading.

TABLE-3
EFFECT OF DIFFERENT LOADING AMOUNTS OF V(V)/MCM-41 CATALYSTS ON YIELD OF PHENOL

V(V)/MCM-41 (wt %)	Conversion (%)	Selectivity (%)
3	12.6	100
5	18.7	100
7	20.9	82

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

TABLE-4
BET DATA FOR DIFFERENT LOADING
AMOUNTS OF V(V)/MCM-41 CATALYSTS

V(V)/MCM-41 (wt %)	Surface area (m ² g ⁻¹)	Total pore volume (mL g ⁻¹)	Average pore diameter (nm)
3	777.4	1.75	2.87
5	755.7	1.64	2.62
7	742.2	1.54	2.54

Effects of metal species on reaction performance under microwave irradiation: The effect of different metal species [*e.g.*, V(V), Cu(II), Co(II)] supported on MCM-41 prepared by impregnated method on the benzene conversion and phenol selectivity at room temperature under microwave irradiation was studied. As shown in Table-5, the activity of metal catalysts followed the order: V(V) > Cu(II) > Co(II). However, BET surface area and pore volume followed the opposite order (as shown in Table-6). This may be due to the V(V) was located more amount on the surface of MCM-41 than Cu(II) and Co(II). Furthermore, it is clear that the type of precursor effect the metal distribution on the surface of catalysts.

TABLE-5
EFFECT OF METAL SPECIES/MCM-41 CATALYSTS PREPARED BY THE IMPREGNATED METHOD ON CATALYTIC ACTIVITY

Catalyst (5 wt %)	Conversion (%)	Selectivity (%)
V(V)/MCM-41	18.7	100
Cu(II)/MCM-41	6.2	93
Co(II)/MCM-41	3.9	91

Reaction conditions: 0.5 g catalyst, 1 mL benzene, 3 mL H₂O₂, 25 mL acetonitrile, 35 °C, 25 min

TABLE-6
BET DATA FOR METAL SPECIES/MCM-41 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)
V(V)/MCM-41	755.7	1.64	2.62
Cu(II)/MCM-41	787.1	1.91	2.82
Co(II)/MCM-41	812.2	2.12	3.35

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

Influence of reaction time: The influence of reaction time on the yield of phenol over V(V)/MCM-41 (5 w/t. %) catalyst at room temperature under microwave irradiation was studied. As shown in Table-7, the yield of phenol was sharply increased to 18.7 % with the increased of reaction time up to 25 min. However, further increase of reaction time to 0.5 h caused the decrease in the yield of phenol. This may be due to the further oxidation of the phenol. So, 25 min is chosen as a suitable reaction time in this work.

Influence of amount of H₂O₂: The influence of H₂O₂ as the oxidant reagent on the yield of phenol was investigated using V(V)/MCM-41 (5 w/t. %) as the catalyst at room temperature under microwave irradiation and the effect of the amount of H₂O₂ on the yield of phenol is shown in Table-8. It is observed that no phenol was obtained without the use of H₂O₂. The yield of phenol increased from 6.1 to 18.7 % with the amount of H₂O₂ increased from 1 to 3 mL. Further increase of the amount of H₂O₂ had a reverse effect on the yield of phenol, which may be due to the further oxidation of the phenol formed with

TABLE-7
EFFECT OF THE REACTION TIME ON CATALYTIC ACTIVITY UNDER MICROWAVE IRRADIATION

Time (min)	Conversion (%)	Selectivity (%)
10	5.8	100
15	8.9	100
20	12.1	100
25	18.7	100
30	21.1	81

Reaction conditions: 0.5 g catalyst, 1 mL benzene, 3 mL H₂O₂, 25 mL acetonitrile, 35 °C

TABLE-8
EFFECT OF THE H₂O₂ AMOUNT ON CATALYTIC ACTIVITY UNDER MICROWAVE IRRADIATION

H ₂ O ₂ (mL)	Conversion (%)	Selectivity (%)
0	0	0
1	6.1	100
2	12.1	100
3	18.7	100
4	22.5	74

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

the presence of excessive amount of H₂O₂, the hydroquinone or benzoquinone was observed. Therefore, 3 mL is considered as a suitable amount in this reaction.

Influence of amount of catalyst: The influence of the amount of the V(V)/MCM-41 (5 w/t. %) catalyst on the yield of phenol at room temperature under microwave irradiation was studied and the results is shown in Table-9. No phenol was detected without the use of the catalyst, which manifested that the V(V) is essential for performing the reducer. The yield of phenol was increased from 6.7 to 18.7 % with the increase amount of the catalyst from 0.1 g to 0.5 g. But a further increase in the amount of the catalyst led to a decrease in the yield of phenol, which may be due to the excessive generation in the hydroxyl free radical with the increase of catalyst amount, inevitably caused opposite effect occurred, decreased the yield of phenol. Therefore, 0.5 g V(V)/MCM-41 (5 w/t. %) is considered as a suitable amount in this reaction.

TABLE-9
EFFECT OF THE CATALYST AMOUNT ON CATALYTIC ACTIVITY UNDER MICROWAVE IRRADIATION

V(V)/MCM-41 (g)	Conversion (%)	Selectivity (%)
0	0	0
0.1	6.7	100
0.3	12.4	100
0.5	18.7	100
0.7	22.9	81

Reaction conditions: 1 mL benzene, 3 mL H₂O₂, 25 mL acetonitrile, 35 °C, 25 min

Conclusion

The direct hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by metal species supported on MCM-41 catalysts at room temperature under microwave irradiation was investigated. The optimum calcined condition for MCM-41 supported is 550 °C calcined temperature and 5 h calcined time. It was found that MCM-41 supported catalysts containing 5 w/t. % V(V) gave the best phenol yield. The activity of different metal species supported on MCM-41

catalyst in production of phenol was V(V) > Cu(II) > Co(II). Compared to conventionally heated method gives phenol yield of 5.8 %, the V(V)/MCM-41 exhibits the higher activity for the conversion of benzene with 18.7 and 100 % selectivity of phenol at the optimum reaction conditions: 1 mL benzene, 25 mL acetonitrile, 0.5 g catalyst, 3 mL 30 % aqueous solution of H₂O₂, 25 min reaction time, 35 °C reaction temperature.

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REFERENCES

1. T. Sakamoto, T. Takagaki, A. Sakakura, Y. Obora, S. Sakaguchi and Y. Ishii, *J. Mol. Catal. Chem.*, **288**, 19 (2008).
2. K. Lemke, H. Ehrich, U. Lohse, H. Berndt and K. Jähnisch, *Appl. Catal. A.*, **243**, 41 (2003).
3. M. Tani, T. Sakamoto, S. Mita, S. Sakaguchi and Y. Ishii, *Angew. Chem. Int. Ed.*, **44**, 2586 (2005).
4. G. Tanarungsun, W. Kiatkittipong, P. Praserttham, H. Yamada, T. Tagawa and S. Assabumrungrat, *Catal. Commun.*, **9**, 1886 (2008).
5. J.K. Joseph, S. Singhal, S.L. Jain, R. Sivakumaran, B. Kumar and B. Sain, *Catal. Today*, **141**, 211 (2009).
6. A.N. Kharat, S. Moosavikia, B.T. Jahromi and A. Badiei, *J. Mol. Catal. Chem.*, **348**, 14 (2011).
7. V.S. Chemyavsky, L.V. Pirutko, A.K. Uriarte, A.S. Kharitonov and G.I. Panov, *J. Catal.*, **245**, 466 (2007).
8. E.J.M. Hensen, Q. Zhu and R.A. Van Santen, *J. Catal.*, **233**, 136 (2005).
9. T. Liu, Y.X. Wang and J.H. Hou, *Asian J. Chem.*, **26**, 745 (2014).
10. T. Liu and J.H. Hou, *Asian J. Chem.*, **26**, 2683 (2014).
11. K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu and Y. Shimizu, *J. Mol. Catal. Chem.*, **114**, 181 (1996).
12. G. Bond, R.B. Moyes and D.A. Whan, *Catal. Today*, **17**, 427 (1993).
13. P. Lidström, J. Tierney, B. Wathey and J. Westman, *Tetrahedron*, **57**, 9225 (2001).