



Microwave-Assisted Hydroxylation of Benzene to Phenol Over Fe(III)/TiO₂ Catalysts at Room Temperature

T. LIU^{1,*}, Y.X. WANG¹ and J.H. HOU²

¹School of Chemistry & 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

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Liquid phase hydroxylation of benzene to phenol with hydrogen peroxide over transition metals supported on TiO₂ catalysts prepared by impregnation method was studied under microwave irradiation. This paper investigated the catalytic performances of TiO₂ supports prepared by various calcined temperature and time. The catalytic activity of Co(II), Cu(II) and Fe(III) metal oxide support on TiO₂ for hydroxylation benzene to phenol was investigated. Coupled conventionally heated method gave phenol yield of 1.5 % and selectivity of 80 %, higher phenol yield of 7.8 % and selectivity of 98 % were obtained when the 5 % loading amounts of Fe(III) under microwave condition. Various reaction parameters, such as reaction time, amount of catalyst and hydrogen peroxide, were investigated to obtain an optimal reaction conditions for phenol formation.

Keywords: Hydroxylation, Phenol, Hydrogen peroxide, TiO₂, Microwave.

INTRODUCTION

Phenol is one of the important chemical intermediates in the broad industrial fields¹. Nowadays approximately 95 % of phenol production was produced by cumene process consisting of three main reaction steps. However, the industrial cumene process has several significant shortcomings *i.e.*, low atom utilization, low phenol yield, high energy consumption and the production of equal amount of acetone as the by product². The direct hydroxylation of benzene to phenol, a one-step reaction, is an attractive alternative for phenol production³.

Many researchers studied that various oxidants⁴⁻⁶, including nitrous oxide⁷, hydrogen peroxide⁸, oxygen⁹, have been employed for the direct oxidation of benzene to phenol. Among them, the hydroxylation of benzene to phenol with hydrogen peroxide was probably the most effective route to achieve high conversion and yield because it is of comparatively low cost and gives only water as a byproduct.

Compared to conventional heating method, an advantage of microwave irradiation is that any substance with high dielectric loss factor can couple easily with microwave radiation and gets heated. Therefore, many reactions that do not occur by conventional heating can proceed under microwave irradiation^{10,11}.

In this study, TiO₂ supports were prepared by the different calcined temperature and time to study the catalytic properties

for hydroxylation of benzene to phenol with hydrogen peroxide at room temperature. The influence of the transition metals [*e.g.* Fe(III), Cu(II) and Co(II)] on phenol yields was investigated. The influence of various reaction parameters on the yield of phenol has also been studied.

EXPERIMENTAL

Catalyst preparation: The purchased chemicals were in analytical grade and used without further purification. The detail procedure for preparation of titania was the following. Tetrabutyl titanate was used as the precursor of titania, anhydrous isopropanol was used as the solvent, and concentrate hydrochloric acid was added to monitor the hydrolysis reaction of tetrabutyl titanate in water. 62 mL of tetrabutyl titanate and 230 mL of anhydrous isopropanol were dissolved in 500 mL beaker, 1.2 mL conc. HCl was added to the above solution under vigorously stirring for 2 min. 13 mL deionized water was added slowly dropwise to the mixed solution with continuous stirring. After standing for 4-5 min, the sol-gel transition took place gradually, and the wet-gels aging for 5-6 days. The drying process of the wet-gels was performed in a vacuum furnace at 50-60 °C for 5 h, the dry-gel powders were heat-treated at various temperatures (*e.g.* 400, 500, 600 °C) and times (*e.g.* 2, 4, 6 h) under oxygen atmosphere (O₂ flow rate: 40 mL min⁻¹) to obtain the nanostructured titania powders.

Catalysts transition metals/TiO₂ were prepared according to the method described by Liu *et al.*¹².

The liquid-phase hydroxylation of benzene was carried out: 1 mL benzene, 15 mL acetonitrile, 35 °C reaction temperature, described amounts of catalyst and H₂O₂ (30 %) along with a magnetical stirrer were added into a 50 mL microwave reactor. The reactor was heated to 35 °C and kept at that temperature for 10-25 min. The reaction mixture was analyzed by gas chromatography.

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-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

Effect of the calcined conditions of TiO₂ on the yield of phenol under microwave irradiation

Effect of calcined temperature: The effect of the calcined temperature (*e.g.* 400, 500, 600 °C) of TiO₂ used as catalysts support on the yield of phenol under microwave irradiation is shown in Table-1. The results reveal that calcined temperature 500 °C of TiO₂ offers the highest conversion. This may be crystal phase of TiO₂ (calcined temperature 500 °C) was converted to the anatase phase. The further increasing calcined temperature to 600 °C, crystal phase of TiO₂ was further converted to the rutile phase. Thus, TiO₂ in anatase phase was selected as a support for all of the following experiments. So, 500 °C is chosen as a suitable calcined temperature.

TABLE-1
EFFECT OF CALCINED TEMPERATURE

Temperature (°C)	Conversion (%)	Selectivity (%)
400	4.5	87
500	7.8	96
600	7.6	86

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H₂O₂, 15 mL acetonitrile, 35 °C, 20 min

Effect of calcined time: The influence of the calcined time (*e.g.* 2, 4, 6 h) of TiO₂ used as catalysts support on benzene conversion and phenol selectivity are summarized in Table-2. The reaction test indicated that at 4 h of the calcined time obtained higher activity. This may be due to the crystal

phase of TiO₂ was perfectly not converted to the anatase phase in a short time, on the other hand, TiO₂ crystal was mainly no activity for the further increasing calcined time to 6 h. Therefore, 4 h is considered as a suitable calcined time.

TABLE-2
EFFECT OF CALCINED TIME

Time (h)	Conversion (%)	Selectivity (%)
2	4.6	95
4	7.8	96
6	6.9	88

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H₂O₂, 15 mL acetonitrile, 35 °C, 20 min

Effect of transition metal species supported on TiO₂ on the yield of phenol under microwave irradiation: The influence of various transition metal species supported on TiO₂ on benzene conversion and phenol selectivity are showed in Table-3. It was found that the activity of transition metal catalysts was ordered as Fe(III) > Cu(II) ≈ Co (II). However, BET surface area and pore volume followed the opposite order (as shown in Table-4). The results indicate that the metal was located more at the surface of TiO₂ than in the pores. In addition, it is clear that the type of precursor influenced the metal distribution in the catalysts.

TABLE-3
EFFECT OF DIFFERENT METAL SALTS/TiO₂ CATALYSTS PREPARED BY IMPREGNATED METHOD ON CATALYTIC ACTIVITY

Catalyst (5 wt %)	Conversion (%)	Selectivity (%)
FeCl ₃ /TiO ₂	7.8	96
Cu(NO ₃) ₂ /TiO ₂	2.7	88
Co(NO ₃) ₂ /TiO ₂	1.2	78

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H₂O₂, 15 mL acetonitrile, 35 °C, 20 min

TABLE-4
BET DATA FOR DIFFERENT METAL SALTS/TiO₂ CATALYSTS PREPARED BY IMPREGNATED METHOD

Catalyst (5 wt %)	Surface area (m ² g ⁻¹)	Total pore volume (mL g ⁻¹)
FeCl ₃ /TiO ₂	71.8	0.25
Cu(NO ₃) ₂ /TiO ₂	79.2	0.30
Co(NO ₃) ₂ /TiO ₂	81.2	0.30

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. The accessibility of metal species into the catalyst pores followed the order Fe(III) > Cu(II) ≈ Co(II). So, Fe(III) is considered as a suitable precursor.

Effect of Fe loading on the yield of phenol under microwave irradiation: The XRD patterns of samples with various percentages of Fe(III) are shown in Fig. 1. No obvious peaks of Fe₂O₃ crystalline phases were found in the 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.

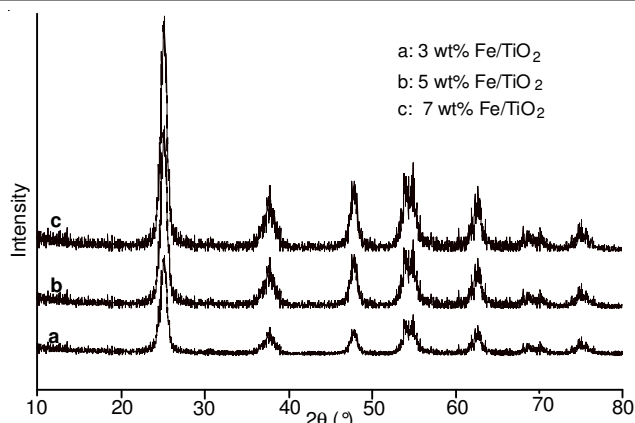


Fig. 1 XRD patterns of different loading contents in FeCl₃/TiO₂ catalysts prepared by impregnated method

The results for the catalytic performances of Fe(III)/TiO₂ catalysts prepared from the three percentages (e.g. 3, 5, 7 wt %) of Fe loading under microwave irradiation are shown in Table-5. It is noticed that the increases in conversion were obtained as a result of the increased amount of metal active species, however, the selectivity of phenol decreased slightly when the amount of Fe loading added to 7 %. This may be due to the deep oxidation of benzene and/or the phenol by the extra catalyst. The specific surface area of the catalysts decreased with increased amount of metal loading (Table-6), indicating that some micropore blockage by metal deposition on pore mouth. So, 5 % is chosen as an optimum Fe loading for all catalysts.

FeCl ₃ /TiO ₂ (wt%)	Conversion (%)	Selectivity (%)
3	4.2	95
5	7.8	96
7	8.3	84

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

FeCl ₃ /TiO ₂ (wt %)	Surface area (m ² g ⁻¹)	Total pore volume (mL g ⁻¹)
3	73.2	0.27
5	71.8	0.25
7	70.4	0.23

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

Effect of the reaction time: The influence of reaction time on the yield of phenol over Fe(III)/TiO₂ (5 wt %) is shown in Table-7. It can be observed that the yield of phenol was sharply increased to 7.8 % 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.

Time (min)	Conversion (%)	Selectivity (%)
10	2.1	87
15	5.2	88
20	7.8	96
25	8.0	89

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H₂O₂, 15 mL acetonitrile, 35 °C, 20 min

Effect of amount of catalyst: The effect of the amount of the Fe (III)/TiO₂ (5 wt %) on the yield of phenol was investigated at room temperature, and the results is shown in Table-8. No phenol was detected without the use of the catalyst, which indicated that catalyst is essential for performing the reducer. The yield of phenol was increased from 0 to 7.8 % with the increase amount of the catalyst. When amount of the catalyst is 0.4 g, the yield of phenol reached 7.8 % with a selectivity of 96 %. But further increase in the amount of the catalyst inversely caused a decrease in the yield of phenol. Therefore, 0.4 g Fe(III)/TiO₂ (5 wt %) is considered as a suitable amount in this reaction.

Amount of catalyst (g)	Conversion (%)	Selectivity (%)
0.2	2.3	81
0.3	5.1	85
0.4	7.8	96
0.5	8.9	80

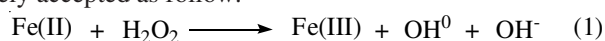
Reaction conditions: 1 mL benzene, 3 mL H₂O₂, 15 mL acetonitrile, 35 °C, 20 min

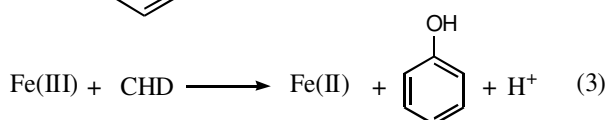
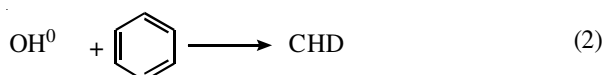
Effect of amount of H₂O₂: The influence of H₂O₂ as the oxidant reagent on the yield of phenol was investigated using Fe(III)/TiO₂ (5 wt %) as the catalyst, and the effect of the amount of H₂O₂ on the yield of phenol is illustrated in Table-9. No phenol was obtained without the use of H₂O₂. The conversion of benzene was found to increase with the increase of the amount of H₂O₂ and reached a maximum value of 7.8 % and selectivity of 96 % at 3 mL. Further increase of the amount of H₂O₂ had a reverse influence on the phenol yield, which result from the further oxidation of the phenol formed, the benzoquinone was observed¹³. Therefore, 3 mL is considered as a suitable amount in this reaction.

Amount of H ₂ O ₂ (mL)	Conversion (%)	Selectivity (%)
1	1.8	84
2	4.8	87
3	7.8	96
4	8.7	77

Reaction conditions: 1 mL benzene, 0.4 g catalyst, 15 mL acetonitrile, 35 °C, 20 min

A classic Fenton-type system for benzene oxidation to phenol catalyzed by Fe(III)/TiO₂ in the presence of H₂O₂ under microwave irradiation. The mechanism of Fenton system is widely accepted as follow:





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 H₂O₂ and metal catalyst added.

Conclusion

The liquid phase hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by transition metals supported on TiO₂ catalysts under microwave irradiation at room temperature was investigated. The optimum calcined condition for TiO₂ supported is 500 °C calcined temperature and 4 h calcined time. TiO₂ supported catalysts containing 3, 5, 7 wt % Fe was tested for their catalytic activity. It was found that 5 wt % gave the best phenol yield. The activity of transition metals supported on TiO₂ catalyst in production of phenol was Fe(III) > Cu(II) ≈ Co(II). The optimum reaction conditions: 1 mL benzene, 15 mL acetonitrile, 0.4 g catalyst, 3 mL 30 % aqueous solution of H₂O₂, 20 min reaction time.

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