



Binary Metal Oxide Supported on TiO₂ Catalysts for Selective Oxidation of Benzene to Phenol Under Microwave Irradiation

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This paper studied the liquid phase hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by binary metal oxide catalysts (V-Cu and V-Co) supported on TiO₂ at room temperature under microwave irradiation. The catalysts were prepared by the impregnated method and characterized by XRD and BET techniques. It was found that the presence of the second metal can improve the phenol production of the typical V/TiO₂ catalyst. TiO₂ loaded with V and Cu of 5 and 5 wt %, respectively, offered the highest yield of phenol. Various reaction parameters, such as solvent type, reaction time, amount of catalyst and hydrogen peroxide, were investigated to obtain an optimal reaction conditions for phenol formation under microwave irradiation.

Keywords: Hydroxylation, Benzene, Hydrogen peroxide, Binary metal oxide, Microwave irradiation.

INTRODUCTION

Phenol has played an important role in the chemical industry as a precursor for chemicals like picric acid, aniline and salicylic acid^{1,2}. Nowadays *ca.* 95 % of phenol production was produced by cumene process consisting of three main reaction steps. However, this process has several disadvantages: high and damaging ecological impact; the production of equal amount of acetone as the by product; the multistep character makes difficult to achieve high phenol yield compared to benzene^{3,4}. Therefore, the study of the direct hydroxylation of benzene to phenol has attracted much attention^{5,6}.

In recent years, this research work focused mainly on mineral acids, simple metal ions and transition metal-based complexes as the well-known traditional catalysts for the selective oxidation of benzene to phenol. Metal ion-exchanged or supported on zeolites, hydrotalcites and resins have been increasingly studied in order to overcome the disadvantage of homogeneous catalysts, recovery and reuse of the catalyst⁷⁻⁹.

Microwave irradiation is well documented to significantly accelerate a wide range of chemical reactions under mild conditions. Compared to conventional heating, microwave irradiation heating has many advantages: no direct contact between the energy source and the reacting chemicals, reducing heat transfer problems, energy efficiency, easy automation and incident power control^{10,11}. Therefore, many reactions that do not occur by conventional heating can proceed under microwave irradiation, especially in a polar system¹².

In the present work, we attempted to improve the catalytic properties of the V/TiO₂ catalyst for the liquid phase hydroxylation of benzene to phenol with hydrogen peroxide at room temperature under microwave irradiation. The second metals (Cu and Co) were loaded together with V on the catalysts for selecting suitable metals for this reaction system. Various techniques were employed to characterize the synthesized catalysts. Finally, the effect of various reaction parameters on the yield of phenol were investigated.

EXPERIMENTAL

All the reagents, including benzene, tetrabutyl titanate, anhydrous isopropanol, methanol, acetone, isopropyl alcohol, ethyl acetate, acetonitrile, NH₄VO₃, Co(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O and H₂O₂ (30 % by weight) were commercially purchased and used without further purification.

Catalyst preparation: The procedure for preparation of TiO₂ was as follows: 62 mL tetrabutyl titanate and 230 mL anhydrous isopropanol were dissolved in 500 mL beaker, 1.2 mL conc. hydrochloric acid 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 500 °C and 4 h under oxygen atmosphere (O₂ flow

rate: 40 mL min⁻¹) to obtain the nanostructured TiO₂ powders. These TiO₂ powders were then impregnated with a mixed solution of metal precursors at room temperature. For example, 5 wt % V and 2.5 wt % Cu loaded on TiO₂ (abbreviated as V₅Cu_{2.5}/TiO₂) were prepared by mixing 10 g of TiO₂, 0.645 g of V (*e.g.*, 1.47 g of ammonium vanadate) and 0.21 g of Cu (*e.g.*, 0.77 g of cupric nitrate). 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 500 °C and 4 h to remove the organic template. After calcination, the catalysts were stored in a dessicator.

Liquid-phase hydroxylation of benzene: 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. In all the experimental runs, 20 mL solvent and 1 mL benzene were used. The reactor was heated to 35 °C for 10-30 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-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 per cent loading of the second metal on catalytic activity under microwave irradiation: The catalytic performance in the hydroxylation of benzene to phenol on the several TiO₂-supported binary metal oxide catalysts (V-Cu/TiO₂, V-Co/TiO₂) at room temperature under microwave irradiation was researched in this work. The formulas of catalysts with different percent metal loadings are abbreviated by using subscripts; for example, V₅Cu₅/TiO₂ represents a catalyst with 5 wt % V and 5 wt % Cu loaded on TiO₂.

The XRD patterns of the catalysts and the blank TiO₂ support were determined (not shown). However, no obvious peaks of V, Cu and Co metals were observed when compared with the pattern of the blank TiO₂. It is probably because of the low metal loading or the oxide being in the amorphous state.

As the summarized in Table-1, 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 from 11.2 % (V₅/TiO₂) to 19.9 % (V₅Cu₅/

TABLE-1
EFFECT OF Cu, Co-V/TiO₂ CATALYSTS PREPARED BY IMPREGNATED METHOD ON CATALYTIC ACTIVITY UNDER MICROWAVE IRRADIATION

Catalyst (wt %)	Conversion (%)	Selectivity (%)
V ₅ /TiO ₂	11.2	95
V ₅ Co _{2.5} /TiO ₂	13.2	91
V ₅ Co ₅ /TiO ₂	15.7	87
V ₅ Co _{7.5} /TiO ₂	17.2	71
V ₅ Cu _{2.5} /TiO ₂	13.4	93
V ₅ Cu ₅ /TiO ₂	19.9	89
V ₅ Cu _{7.5} /TiO ₂	21.1	70

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 4 mL H₂O₂, 20 mL acetonitrile, 35 °C, 25 min.

TiO₂) and 15.7 % (V₅Co₅/TiO₂), however, the phenol selectivity significantly reduced. The decrease of the phenol selectivity at high metal loading could be due to the reduction of dispersion of the catalyst metal. 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 optimum percent loading of Cu and Co which offered the highest phenol yield was 5 wt % (V₅Cu₅/TiO₂).

TABLE-2
BET DATA FOR Cu, Co-V/TiO₂ CATALYSTS PREPARED BY IMPREGNATED METHOD

Catalyst (wt %)	Surface area (m ² g ⁻¹)	Total pore volume (mL g ⁻¹)
V ₅ /TiO ₂	69.7	0.25
V ₅ Co _{2.5} /TiO ₂	67.5	0.24
V ₅ Co ₅ /TiO ₂	64.2	0.23
V ₅ Co _{7.5} /TiO ₂	60.4	0.22
V ₅ Cu _{2.5} /TiO ₂	65.7	0.23
V ₅ Cu ₅ /TiO ₂	60.1	0.21
V ₅ Cu _{7.5} /TiO ₂	58.7	0.20

Effect of operating parameters on the hydroxylation of benzene to phenol under microwave irradiation

Effect of solvent type on the yield of phenol: In the reaction system of oxidation of benzene with hydrogen peroxide, solvent was used to reduce the reactants transfer resistance by helping to dissolve H₂O₂ into the benzene phase. A volume of 20 mL of various solvents was added. The catalytic performance of the system with various solvents (*e.g.*, acetonitrile, methanol, acetone, isopropyl alcohol and ethyl acetate) over V₅Cu₅/TiO₂ catalyst at room temperature under microwave irradiation is shown in Table-3. It was noted that acetonitrile as solvent gave obviously higher conversion than other solvent. That may be due to acetonitrile has a greater affinity to the catalytic surface than other solvents, which could lead to more effective transport of the reactants to the catalyst active sites under microwave irradiation. Thus, we focus our attention on acetonitrile as the solvent in this reaction.

Effect of the reaction time on the yield of phenol: The influence of reaction time on the yield of phenol over V₅Cu₅/TiO₂ catalyst at room temperature under microwave irradiation is illustrated in Table-4. It can be observed that conversion of benzene increased significantly with reaction time until 25 min from 7.8 to 19.9 % and after that, the conversion of benzene increased slightly and the selectivity of phenol decreased sharply with further increase of the reaction time to 30 min,

TABLE-3
EFFECT OF SOLVENT TYPE ON REACTION
UNDER MICROWAVE IRRADIATION

Solvent	Conversion (%)	Selectivity (%)
Acetonitrile	19.9	89
Methanol	10.4	82
Acetone	7.7	84
Isopropyl alcohol	3.9	79
Ethyl acetate	5.6	81

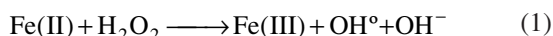
Reaction conditions: 0.4 g catalyst, 1 mL benzene, 4 mL H₂O₂, 20 mL solvent, 35 °C, 25 min.

TABLE-4
EFFECT OF THE REACTION TIME ON REACTION
UNDER MICROWAVE IRRADIATION

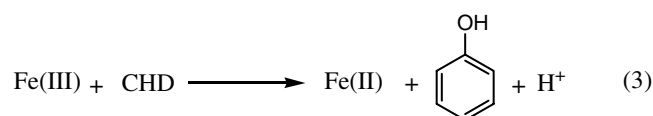
Time (min)	Conversion (%)	Selectivity (%)
10	7.8	95
15	10.4	92
20	12.7	90
25	19.9	89
30	21.6	71

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 4 mL H₂O₂, 20 mL acetonitrile, 35 °C.

which is due to the further oxidation of phenol. Thus, 25 min is considered as a suitable reaction time in this work. The reaction occurs similar to Fenton chemistry, through the participation of hydroxyl radical in activating benzene toward the formation of phenol. The mechanism of Fenton system is widely accepted as follows¹³:



The hydroxyl radical reacts directly with benzene to produce cyclohexadienyl (CHD) radical, which subsequently undergoes an H⁺ abstraction as follows:



Effect of the amount of H₂O₂ for the hydroxylation of benzene: The influence of H₂O₂ as the oxidant reagent on the yield of phenol was investigated using V₅Cu₅/TiO₂ as the catalyst and the effect of the amount of H₂O₂ on the yield of phenol at room temperature under microwave irradiation is illustrated in Table-5. It is obvious that no phenol was obtained without the use of H₂O₂, indicating that the presence of H₂O₂ is essential for performing the oxidant in this reaction. When the amount of H₂O₂ increased from 1 to 4.0 mL, the conversion of benzene increased significantly from 6.4 to 19.9 %. However, further increase of the amount of H₂O₂ had a reverse influence on the phenol yield. It can be explained that further oxidation of phenol to hydroquinone and benzoquinone can be occurred with the presence of excessive amount of H₂O₂ oxidant. The use of high amount of H₂O₂ resulted in high amount of hydroxyl radical in the reaction, but excessive hydroxyl radical caused a problem on further oxidation of phenol to byproducts. So, 4 mL is considered as a suitable amount in this reaction.

TABLE-5
EFFECT OF THE H₂O₂ AMOUNT ON REACTION
UNDER MICROWAVE IRRADIATION

H ₂ O ₂ (mL)	Conversion (%)	Selectivity (%)
0	0	0
1	6.4	97
2	10.7	94
3	13.4	92
4	19.9	89
5	23.5	70

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 20 mL acetonitrile, 35 °C, 25 min.

Effect of amount of catalyst for hydroxylation of benzene: Effect of the amount of V₅Cu₅/TiO₂ catalyst on the yield of phenol was investigated at 35 °C under microwave irradiation and the results is shown in Table-6. It was found that no phenol was detected without the use of V₅Cu₅/TiO₂ catalyst, which indicated that V₅Cu₅/TiO₂ catalyst is essential for performing the reducer. The conversion of benzene was increased from 7.8 to 19.9 % with the increase amount of the V₅Cu₅/TiO₂ catalyst from 0.2-0.4 g. On the other hand, a further increase in the amount of catalyst to 0.5 g caused a decrease in the yield of phenol. This may be due to the oxidation of phenol by the extra catalyst. Increasing amount of catalyst cause the increase of the hydroxyl free radical generation, but an excess of hydroxyl free radical generated inevitably promoted phenol side effects occurred, reduced the yield of phenol. Therefore, 0.4 g is chosen as a suitable amount in this reaction.

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

Catalyst (g)	Conversion (%)	Selectivity (%)
0	0	0
0.2	7.8	94
0.3	11.4	91
0.4	19.9	89
0.5	22.7	71

Reaction conditions: 1 mL benzene, 4 mL H₂O₂, 20 mL acetonitrile, 35 °C, 25 min.

Conclusion

The hydroxylation of benzene to phenol with hydrogen peroxide was performed at room temperature under microwave irradiation using various V-containing binary metal oxide supported on TiO₂ catalysts. The second metal can improve the phenol production of the typical V/TiO₂ catalyst. V₅Cu₅/TiO₂ catalyst was found to exhibit the highest activity for hydroxylation of benzene to phenol than other catalysts. The highest yield of phenol was achieved in the optimum condition under microwave irradiation: 0.4 g catalyst, 1 mL benzene, 20 mL acetonitrile, 4 mL 30 % aqueous solution of H₂O₂, 25 min reaction time, 35 °C reaction temperature.

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