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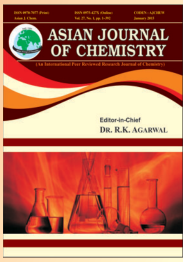

Direct Hydroxylation of Benzene to Phenol over V/β-Zeolite as Catalysts Under Microwave Irradiation

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Direct hydroxylation of benzene to phenol with hydrogen peroxide over catalysts prepared by the V(V) impregnated on β-zeolite was examined under microwave irradiation. It was found that the V(V)/β-zeolite catalyst gave the highest activity than Cu(II), Co (II)/β-zeolite at same experimental condition. Various techniques (XRD and BET surface area) were employed to characterize the catalysts. The influence of some operating variables, such as the amount of hydrogen peroxide used, the amount of catalyst used and the reaction time on the conversion of benzene, were studied to obtain the optimal reaction conditions under microwave irradiation. A benzene conversion of 14.7 % with a selectivity of 100 % was obtained when the 5 % loading amount of V(V) under optimized conditions.

Keywords: Hydroxylation, Benzene, Hydrogen peroxide, V(V)/β-zeolite.

INTRODUCTION

Phenol is one of the important chemical intermediates for the manufacture of agrochemicals, petrochemicals and polymers[1,2]. Nowadays more than 90 % of the world production was produced by cumene process consisting of three main reaction steps. However, this process has several disadvantages *e.g.*, low atom utilization, low phenol yield, high energy consumption and the production of equal amount of acetone as the by product[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 finding a suitable supported catalyst for the selective oxidation of benzene to phenol under mild reaction conditions with H_2O_2 as an oxidant. Many researchers studied the oxidation of benzene to phenol by using the transition metal oxide catalysts supported on SiO_2, Al_2O_3, TiO_2, MCM-41, activated carbon[7,8]. Compared to conventional heating method, microwave irradiation heating has many advantages, such as increasing energy efficiency, reducing the problems of low heat transfer and easy automation and incident power contro[l9,10]. So, many chemical reactions that do not occur by conventional heating can proceed under microwave irradiation[11].

In the present work, the hydroxylation of benzene to phenol was investigated over V(V)/β-zeolite catalyst prepared by the impregnated method under microwave irradiation. Various metal [*e.g.*, Cu(II) and Co(II)] were loaded on the β-zeolite support and the catalytic performance of the obtained catalysts was compared. In addition, various techniques were employed to characterize the synthesized catalysts. Finally, we have also studied the influence of various parameters such as the amount of hydrogen peroxide used, the amount of catalyst used and the reaction time on the yield of phenol.

EXPERIMENTAL

All the reagents, including β-zeolite (200 mesh), benzene, NH_4VO_3, $Cu(NO_3)_2·3H_2O$, $Co(NO_3)_2·6H_2O$, H_2O_2 (30 % by weight) and acetonitrile, were commercially purchased and used without further purification.

Procedure for the preparation of metal oxides/β-zeolite catalyst by impregnated method was as follows: an aqueous solution which dissolved the prescribed amounts of metallic salt and β-zeolite is stirred for 2 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 various temperatures (*e.g*. 400, 500, 600 °C) and times (*e.g*. 2, 4, 6 h) under oxygen atmosphere (O_2 flow rate: 40 mL min^{-1}) 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, 70 °C, described amounts catalyst and H_2O_2 were added into a 50 mL CEM discover microwave reactor with a magnetical stirrer. The reactor was kept for 5-25 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.

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* 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:

$$\text{Yield of phenol} = \frac{\text{mole of phenol produced}}{\text{initial mol of benzene}}$$

$$\text{Selectivity of phenol} = \frac{\text{mole of phenol produced}}{\text{mol of benzene reacted}}$$

RESULTS AND DISCUSSION

Evaluation of performances of the catalysts preparation conditions:

Effect of the calcined temperature: The results for the effect of the calcined temperature (*e.g.* 400, 500, 600 °C) of 5 % (w/t) V(V)/β-zeolite catalysts prepared by the impregnated method on the yield of phenol are shown in Table-1. All the catalysts are calcined for 4 h. It is found that calcined temperature 500 °C of V(V)/β-zeolite catalyst offers the highest conversion of benzene than other calcined temperature. So, 500 °C is chosen as a suitable calcined temperature.

TABLE-1
EFFECT OF CALCINED TEMPERATURE

Temperature (°C)	Conversion (%)	Selectivity (%)
400	9.1	100
500	14.3	100
600	10.7	100

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 20 min

Effect of calcined time: The influence of the calcined time (*e.g.* 2, 4, 6 h) of V(V)/β-zeolite catalysts on benzene conversion and phenol selectivity are summarized in Table-2. The results indicate that at 4 h of the calcined time obtained higher activity than other calcined time. This may be due to the crystal phase of catalyst was perfectly not converted in a short time. However, catalyst was mainly no activity for the further increasing calcined time to 6 h because of crystal reunion. Therefore, 4 h is considered as a suitable calcined time.

TABLE-2
EFFECT OF CALCINED TIME

Time (h)	Conversion (%)	Selectivity (%)
2	10.2	100
4	14.7	100
6	11.1	97

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 20 min

Effect of V(V) loading: The XRD patterns of samples with various percentages of V(V)/β-zeolite catalysts prepared by impregnated method are shown in Fig. 1. It is noticed that no obvious peaks of V_2O_5 crystalline phases was observed in the XRD patterns, indicating that no bulk metal oxide was presented in all catalysts, which could be due to a low loading or the oxide being in the amorphous state. The influence of the different loading amount of V(V) (*e.g.*, 3, 5 and 7 %) on the benzene conversion and phenol selectivity was investigated. As shown in Table-3, the increasing of the V(V) loadings improved the benzene conversion; however, the phenol selectivity obviously reduced, thus an optimum yield of 5 % was observed. The increases in conversion may be due to the increasing amount of metal active species, however, the excessive metal species reduces of dispersion of the catalyst metal.

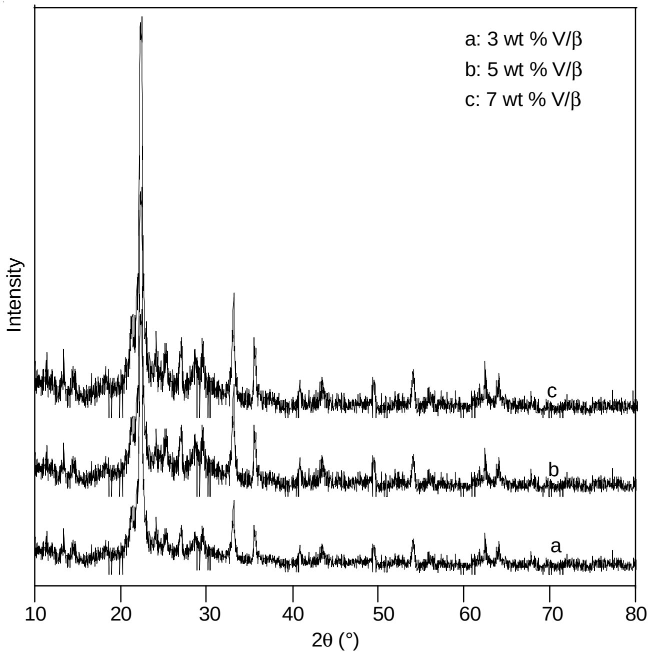

Fig. 1. XRD patterns of V(V)/β-zeolite prepared by the impregnated method

TABLE-3
EFFECT OF DIFFERENT LOADED AMOUNT IN V(V)/β-ZEOLITE CATALYSTS PREPARED BY THE IMPREGNATED METHOD ON CATALYTIC ACTIVITY

V(V)/β-zeolite (wt. %)	Conversion (%)	Selectivity (%)
3	10.2	100
5	14.7	100
7	15.9	86

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 20 min

The specific surface area of the catalysts decreased with increased amount of V(V) loading (Table-4), manifesting

TABLE-4
BET DATA FOR DIFFERENT LOADED AMOUNT IN V(V)/β-ZEOLITE CATALYSTS PREPARED BY THE IMPREGNATED METHOD

V(V)/β-zeolite (wt. %)	Surface area ($m^2 g^{-1}$)	Total pore volume (mLg^{-1})	Average pore diameter (nm)
3	318.7	0.38	4.56
5	315.4	0.35	4.52
7	311.1	0.33	4.50

that some micropore blockage by metal deposition on pore mouth. Thus, 5 % was selected as an optimum V(V) loading.

Effects of metal species on reaction performance under microwave irradiation: The influence of different metal species [*e.g.*, V(V), Cu(II), Co(II)}] supported on β-zeolite prepared by the same experimental condition on benzene conversion and phenol selectivity are summarized in Table-5. It was found that 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 (Table-6). This could be due to V(V) was located more at the surface of β-zeolite than Cu(II) and Co(II). In addition, it is clear that type of precursor influenced the metal distribution in catalysts.

TABLE-5
EFFECT OF DIFFERENT METAL SPECIES/β-ZEOLITE CATALYSTS PREPARED BY THE IMPREGNATED METHOD ON CATALYTIC ACTIVITY

Catalyst (5 wt. %)	Conversion (%)	Selectivity (%)
V(V)/β-zeolite	14.7	100
Cu(II)/β-zeolite	5.1	90
Co(II)/β-zeolite	3.5	85

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 20 min

TABLE-6
BET DATA FOR DIFFERENT METAL SPECIES/β-ZEOLITE 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)/β-zeolite	315.4	0.35	4.52
Cu(II)/β-zeolite	328.1	0.41	4.62
Co(II)/β-zeolite	334.2	0.44	4.65

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

Effect of reaction time: The effect of reaction time on the conversion of benzene and yield of phenol over V(V)/β-zeolite (5 wt.%) catalyst under microwave irradiation is shown in Table-7. It is obvious that the reaction time increased from 5 to 20 min, the yield of phenol increased sharply from 3.1 to 14.7 %. However, the yield decreased with the further increase of reaction time, which maybe due to the further oxidation of phenol. Thus, 20 min is considered as a suitable reaction time in this work.

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

Time (min)	Conversion (%)	Selectivity (%)
5	3.1	100
10	7.5	100
15	10.2	100
20	14.7	100
25	16.2	87

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

Effect of amount of catalyst: The influence of amount of V(V)/β-zeolite (5 wt. %) catalyst on the yield of phenol was studied under microwave irradiation and the results is shown in Table-8. It is obvious that no phenol was detected without the use of V(V)/β-zeolite catalyst, indicating that the presence of V(V) essential for performing the reducer in this reaction. The yield of phenol was increased greatly from 2.1 to 14.7 % when the amount of catalyst increased from 0.1 to 0.4 g. But further increase in the amount of the catalyst inversely caused a decrease in the yield of phenol. It maybe due to the increasing amount of catalyst, will cause the increasing in the hydroxyl free radical generation and thus to enhance the yield of phenol; but an excess of hydroxyl free radical generated inevitably leaded to phenol secondary reaction occured, reduced the yield of phenol. Therefore, 0.4g V(V)/β-zeolite (5 w/t. %) is considered as a suitable amount in this reaction.

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

V(V)/β-zeolite (g)	Conversion (%)	Selectivity (%)
0	0	0
0.1	3.4	100
0.2	7.8	100
0.3	11.2	100
0.4	14.7	100
0.5	17.2	81

Reaction conditions: 1 mL benzene, 3 mL H_2O_2, 15 mL acetonitrile, 70 °C, 20 min

Effect of amount of H_2O_2: The effect of H_2O_2 as oxident reagent on the yield of phenol was studied using V(V)/β-zeolite (5 w/t.%) as catalyst and the influence of amount of H_2O_2 on the yield of phenol under microwave irradiation is shown in Table-9. It is found that no phenol was detected in absence of H_2O_2, indicating that H_2O_2 as oxidant is essential present in the reaction system. The yield of phenol was found to increase with the increase of amount of H_2O_2 and reached a maximum value of 14.7 % at 3 mL. However, further increase of amount of H_2O_2 had a reverse influence on the phenol yield, which maybe due to the further oxidation of phenol formed, such as benzoquinone. So, 3 mL is considered as a suitable amount in this reaction.

TABLE-9
EFFECT OF THE H_2O_2 AMOUNT ON CATALYTIC ACTIVITY UNDER MICROWAVE IRRADIATION

H_2O_2 (mL)	Conversion (%)	Selectivity (%)
0	0	0
1	5.5	100
2	9.7	100
3	14.7	100
4	17.5	78

Reaction conditions: 0.4 g catalyst, 1 mL benzene, 15 mL acetonitrile, 70 °C, 20 min

Conclusion

The liquid phase hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by V(V) supported on β-zeolite catalysts prepared by the impregnated method under microwave irradiation was investigated. The optimum calcined condition for V(V)/β-zeolite is 500 °C calcined temperature and 4 h calcined time, 5 % of loading amount of V(V) gave the best phenol yield. The activity of different metals salts supported on β-zeolite catalyst in production of phenol was V(V) > Cu(II) > Co(II). The V(V)/β-zeolite prepared under optional preparation conditons exhibits the high activity for the conversion of benzene with 14.7 and 100 % selectivity of phenol at the optimum reaction conditions: l mL benzene, 15 mL acetonitrile, 0.4 g catalyst, 3 mL 30 % aqueous solution of H_2O_2, 20 min reaction time, 70 °C reaction temperature.

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