Asian Journal of Chemistry; Vol. 27, No. 7 (2015), 2489-2491

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17944

Low Temperature Hydroxylation of Benzene to Phenol Over SiO_2 as Supported Catalysts Under Microwave Irradiation

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Received: 5 May 2014; *Accepted*: 30 June 2014; *Published online*: 30 March 2015; AJC-17063

This paper investigated the microwave assisted liquid phase hydroxylation of benzene to phenol with hydrogen peroxide over V(V)/SiO_2 catalysts prepared by microwave impregnated method. The catalysts were characterized by XRD, N_2 adsorption techniques. The results manifested that the performance of the catalysts was significantly affected by the amount of V(V) loaded onto the SiO_2 and microwave irradiation time. The effects of various reaction parameters, such as the amount of catalyst used, the amount of hydrogen peroxide used and reaction time on the yield of phenol was investigated at room temperature under microwave irradiation. Coupled conventionally heated method gives phenol yield of 11.8 %, the V(V)/SiO_2 prepared by microwave impregnated method gives higher phenol yield of 19.7 % and selectivity of 100 % under microwave irradiation.

Keywords: Microwave assisted, Hydroxylation, Benzene; V(V)/SiO_2.

INTRODUCTION

Phenol is one of the most important chemicals in industry and widely used in the fields of resins, fibers and medicines[1-3]. Currently, most of the worldwide production of phenol is now based on the "cumene process", consisting of three main reaction steps. However, this process has several disadvantages *i.e.*, low atom utilization, low phenol yield, high energy consumption and the production of equal amount of acetone as the by product[4,5]. Consequently, this situation has prompted scientists to develop other methods for producing phenol from benzene, preferably *via* a single-step and free of co-product(s) reaction[6,7]. In recent years, microporous and mesoporous materials as the promising supports have been reported for the liquid-phase hydroxylation process with clean oxidant H_2O_2, such as the transition metal oxide catalysts supported on SBA-16, Al_2O_3, TiO_2, MCM-41, activated carbon[8-10].

Compared to conventional heating method, microwave irradiation is well documented to significantly accelerate a wide range of chemical reactions, especially in a polar system, under mild conditions. Moreover, microwave irradiation has many advantages, such as no direct contact between the energy source and the reacting chemicals, increasing energy efficiency, reducing heat transfer problems, easy automation and incident power control[11-13].

In the present work, microwave assisted the hydroxylation of benzene to phenol was investigated over V(V)/SiO_2 prepared by the microwave impregnated method and indicated that the performance of the catalysts was significantly affected by the amount of V(V) loaded onto the SiO_2 and microwave irradiation time. In addition, various techniques were employed to characterize the synthesized catalysts. Finally, we also explored the optimal reaction conditions for phenol formation at room temperature under microwave irradiation, obtained phenol yield of 19.7 % and selectivity of 100 %.

EXPERIMENTAL

Materials and catalyst preparation: All the reagents, including benzene, NH_4VO_3, $FeCl_3·6H_2O$, $Cu(NO_3)_2·3H_2O$, H_2O_2 (30 % by weight) and acetonitrile, were commercially purchased and used without further purification.

The procedure for the preparation by the microwave impregnated method was as follows: The aqueous solution which dissolved the prescribed amounts of NH_4VO_3 and SiO_2 along with a magnetical stirrer were placed into a 100 mL CEM discover microwave reactor. The reactor was heated to 80 °C and kept at that temperature for 5-30 min. Then the solution containing precipitates was filtrated and the solid product obtained was further dried at 70 °C overnight *in vacuum* oven. The catalysts were stored in a dessicator.

Catalytic tests: The liquid-phase hydroxylation of benzene was carried out: 1 mL benzene, 35 °C reaction temperature, described amounts of solvent, catalyst and H_2O_2 were added into a 50 mL CEM discover microwave reactor with a magnetical stirrer. The reactor was heated to 35 °C and kept at that temperature for 5-20 min. The reaction mixture was analyzed with a Hewlett-Packard 6890/5973 GC/MS equipped with a capillary column coated with HP-5MS (cross-link 5 % PH ME siloxane, 30 m × 0.32 mm i.d., 0.25 μm film thickness) and a quadrupole analyzer and operated in electron impact (70 eV) mode. The mass range scanned was from 30 to 500 amu. Data were acquired and processed using Chemstation software. The compounds were identified by comparing mass spectra with NIST05 library data.

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 measurements were carried out with a D/max-RA X-ray diffractometer (Rigaku, Japan), CuK$_\alpha$ 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-1 MP 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

Evaluation of performances of catalysts preparation conditions

Effects of transition metal species: The transition metal/SiO_2 catalysts were prepared by microwave impregnated method from three precursors *i.e.*, NH_4VO_3, $FeCl_3$, $Cu(NO_3)_2$. The influence of the catalytic activity of the different transition metal species supported SiO_2 on the benzene conversion and phenol selectivity under microwave irradiation are summarized in Table-1. The results reveal that the activity of different transition metal catalysts followed the order V(V) > Fe(III) > Cu(II). However, BET surface area and pore volume followed the opposite order (as shown in Table-2). The results indicate that the metal V(V) was located larger amount on the surface of SiO_2 than Fe(III) and Cu(II). It is known that the catalytic activity of the transition metal species is dependent on the outer *d* electron density. The electron density of V(V) is lesser than Fe(III) and Cu(II). So, the capacity of V(V) to activate oxidant species is greater. Meanwhile, the accessibility of metal species into the catalyst pores followed the order V(V) > Fe(III) > Cu(II). Therefore, V(V) is considered as a suitable precursor.

Effect of the V(V) loading: The XRD patterns of samples with various amounts (*e.g.*, 0.5 mmoL, 1 mmoL, 1.5 mmoL) of V(V)/SiO_2 are determined. However, no obvious peaks of V_2O_5 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 (not shown).

TABLE-1
EFFECT OF THE TRANSITION METAL SPECIES/SiO_2 CATALYSTS PREPARED BY MICROWAVE IMPREGNATED METHOD ON CATALYTIC ACTIVITY

Catalyst (1 mmoL)	Conversion (%)	Selectivity (%)
NH_4VO_3/SiO_2	19.7	100
$FeCl_3/SiO_2$	15.2	100
$Cu(NO_3)_2/SiO_2$	7.5	95

Reaction conditions: 1.5 g catalyst, 1 mL benzene, 1.5 mL H_2O_2, 15 mL acetonitrile, 35 °C, 15 min

TABLE-2
BET DATA FOR THE TRANSITION METAL SPECIES/SiO_2 PREPARED BY MICROWAVE IMPREGNATED METHOD

Catalyst (1 mmoL)	Surface area ($m^2 g^{-1}$)	Total pore volume (mL g^{-1})
NH_4VO_3/SiO_2	349.1	0.65
$FeCl_3/SiO_2$	358.8	0.68
$Cu(NO_3)_2/SiO_2$	371.2	0.71

The results for the catalytic performances of V(V)/SiO_2 catalysts prepared from the three amounts (*e.g.*, 0.5 mmoL, 1 mmoL, 1.5 mmoL) of V(V) loading under microwave irradiation are shown in Table-3. It is noticed that the benzene conversion increased with increasing the amount of V(V) loaded, however, the selectivity of phenol decreased slightly when the amount of V(V) loading added to 1.5 mmoL. It is because phenol can be further reacted to give catechol, benzoquinone and hydroquinone, which are undesirable byproducts. The specific surface area of the catalysts decreased with increased amount of metal loading (Table-4), indicating that some micropore blockage by metal deposition on pore mouth. Thus, 1 mmoL is choosen as an optimum V(V) loading for all catalysts.

TABLE-3
EFFECT OF THE DIFFERENT LOADING CONTENTS IN NH_4VO_3/SiO_2 CATALYSTS PREPARED BY MICROWAVE IMPREGNATED METHOD ON THE YIELD OF PHENOL

NH_4VO_3/SiO_2 (mmoL)	Conversion (%)	Selectivity (%)
0.5	11.7	100
1.0	19.7	100
1.5	21.5	83

Reaction conditions: 1.5 g catalyst, 1 mL benzene, 1.5 mL H_2O_2, 15 mL acetonitrile, 35 °C, 15 min

TABLE-4
BET DATA FOR THE DIFFERENT LOADING CONTENTS IN NH_4VO_3/SiO_2 CATALYSTS PREPARED BY MICROWAVE IMPREGNATED METHOD

NH_4VO_3/SiO_2 (mmoL)	Surface area ($m^2 g^{-1}$)	Total pore volume (mL g^{-1})
0.5	360.8	0.68
1.0	349.1	0.65
1.5	339.2	0.61

Effect of the microwave irradiation time: The effect of the microwave irradiation time over V(V)/SiO_2 catalysts prepared by microwave impregnated method at 80 °C on the conversion of benzene was investigated and the results is shown in Table-5. Increasing of microwave irradiation time from 5

TABLE-5
EFFECT OF THE MICROWAVE
IRRADIATION TIME ON CATALYTIC ACTIVITY

Time (min)	Conversion (%)	Selectivity (%)
5	7.8	100
10	13.2	100
20	19.7	100
30	15.0	100

Reaction conditions: 1.5 g catalyst, 1 mL benzene, 1.5 mL H_2O_2, 15 mL acetonitrile, 35 °C, 15 min

to 20 min, the conversion of benzene was found to increase from 7.8 to 19.7 %. However, further increased to 0.5 h, the conversion of benzene decreased significantly. Thus, 20 min is considered as a suitable irradiation time.

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

Effect of the catalyst amount on the yield of phenol: The results for the effect of the amount of catalyst on the yield of phenol investigated over V(V)/SiO_2 prepared by microwave impregnated method at room temperature under microwave irradiation is shown in Table-6. It was indicated that the catalyst amount increased from 0.5 to 1.5 g, the conversion of benzene increased sharply from 7.7 to 19.7 %, but a further increase in the amount of catalyst inversely caused a decrease in the selectivity of phenol, which result from the further oxidation of the phenol formed, the benzoquinone was formed. Therefore, 1.5 g V(V)/SiO_2 is considered as a suitable amount in this reaction.

TABLE-6
EFFECT OF THE CATALYST
AMOUNT ON THE YIELD OF PHENOL

NH_4VO_3/SiO_2 (g)	Conversion (%)	Selectivity (%)
0.5	7.7	100
1.0	12.1	100
1.5	19.7	100
2.0	22.5	81

Reaction conditions: 1 mL benzene, 1.5 mL H_2O_2, 15 mL acetonitrile, 35°C, 15 min

Effect of the amount of H_2O_2 for the hydroxylation of benzene: The effect of the amount of H_2O_2 for the hydroxylation of benzene on the yield of phenol over V(V)/SiO_2 prepared by microwave impregnated method at room temperature under microwave irradiation is shown in Table-7. When the amount of H_2O_2 increased from 0.5 to 1.5 mL, the yield of phenol increased from 5.2 to 19.7 %. However, when the amount of H_2O_2 was further up to 2 mL, the yield of phenol dropped quickly. It can be explained that further oxidation of phenol to hydroquinone or benzoquinone can be occurred with the presence of excessive amount of H_2O_2 oxidant. So, 1.5 mL is considered as a suitable amount in this reaction.

TABLE-7
EFFECT OF THE H_2O_2 AMOUNT ON THE YIELD OF PHENOL

H_2O_2 (moL)	Conversion (%)	Selectivity (%)
0.5	5.2	100
1.0	12.3	100
1.5	19.7	100
2.0	22.5	77

Reaction conditions: 1.5 g catalyst, 1 mL benzene, 15 mL acetonitrile, 35 °C, 15 min

TABLE-8
EFFECT OF THE REACTION TIME ON THE YIELD OF PHENOL

Time (min)	Conversion (%)	Selectivity (%)
5	6.8	100
10	13.7	100
15	19.7	100
20	21.5	81

Reaction conditions: 1.5 g catalyst, 1 mL benzene, 1.5 mL H_2O_2, 15 mL acetonitrile, 35 °C

Effect of the reaction time on the yield of phenol: The effect of reaction time on the yield of phenol over V(V)/SiO_2 prpeared by microwave impregnated method at room temperature under microwave irradiation is shown in Table-8. It can be observed that the conversion of benzene increased significantly from 6.8 to 19.7 % when the reaction time increased from 5 to 15 min and after that, the yield decreased sharply with the further increase of reaction time to 20 min. This may be caused by the further oxidation of the phenol. So, 15 min is chosen as a suitable reaction time in this reaction.

Conclusion

The liquid phase hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by V(V) supported on TiO_2 catalysts prepared microwave impregnated method under microwave irradiation at room temperature was investigated. The optimum preparation condition for V(V)/SiO_2 is 1 m moL loading amount and 20 microwave irradition time. The activity of transition metals supported on SiO_2 catalyst in production of phenol was V(V) > Fe (III) > Cu(II). Compared to conventionally heated method gives phenol yield of 11.8 %, the V(V)/SiO_2 prepared by the microwave impregnated method gives higher phenol yield of 19.7 % and selectivity of 100 % at the optimum reaction conditions: l mL benzene, 15 mL acetonitrile, 1.5 g catalyst, 1.5 mL 30 % aqueous solution of H_2O_2, 15 min reaction time, 35 °C reaction temperature.

ACKNOWLEDGEMENTS

The authors are grateful to the Natural Science Foundation of China (Projects 51374205) for the financial support.

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