# VAPOR PHASE OXIDATION OF BENZOIC ACID TO PHENOL USING NICKEL-IRON OXIDES CATALYSTS

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## ABSTRACT

*$NiO$ and $Fe_2O_3$ were found to show the catalytic activities for the vapor phase oxidation of benzoic acid to form phenol. Furthermore, the enhancement of the activity and phenol selectivity were achieved by combined Ni and Fe components prepared by precipitation. The calcination temperature and the atomic ratio of Ni to Fe were found to be important for the enhancement of activity.*

## INTRODUCTION

Phenol is one of the most important starting material for various chemical products, such as phenol resin, bis-phenol A, aniline and some agriculture chemicals.

Although, a number of methods for phenol synthesis have been proposed, the cumene is now used as the main route for commercial production of phenol. In the process, cumene is first synthesized from benzene and propylene, and then oxidized to cumene hydroperoxide, followed by the decomposition to phenol and acetone by acid catalyst. The process is estimated to be very cost effective because of its mild reaction conditions and high yield of phenol [1]. In addition, acetone, which is also a commercially important chemical, is coproduced with phenol in the process. However, a problem has arisen: the future demand for acetone will decrease, while the demand for phenol will enormously increase. The imbalance of demand between phenol and acetone has caused the Dow process to be recognized as an alternative for phenol production. In the Dow process, toluene is first oxidized to benzoic acid using cobalt-manganese catalyst, and then the benzoic acid is converted to phenol. According to some literature, the copper catalysts for the latter reaction have problems such as low yield of phenol, tar formation and catalyst deactivation. In spite of the attempts to improve the copper-based catalyst, these problems remain unsolved at present, necessitating the development of a more efficient catalyst [2,10].

In this paper, we attempt to obtain a more efficient catalyst that consists of nickel and iron oxides.

## EXPERIMENTAL WORK

### Catalysts

Nickel and iron components prepared by precipitation method with aqueous solutions of metal nitrates and sodium hydroxide (BDH limited Company) were also used for the precipitation of $NiO$, $Fe_2O_3$ combined catalysts.

The precipitate obtained were washed with pure water until they become free from sodium and then dried in air at a temperature of 110°C (383°K) for 25 hr and then calcined again in air at a temperature range of 400-800°C (673-1073°K) for 3 hr (9).

### Apparatus and Procedure

The feed was heated prior to entrance into the reactor. The heating section is divided into three separate sections; steam generator, air heater using heating tape and round bottom flask heated by a mantle heater to heat the benzoic acid. Heating is controlled by voltage regulators.

The reaction system was a laboratory bench scale made of QVF glass with an inner diameter of 2.54 cm and a length of 50-70 cm. The reactor is divided into two zones. The entrance zone (30 cm long), serving as a preheater section, was packed with glass balls. The reaction zone, the length of which depends on the space velocity, was packed with the catalyst. Both zones are heated with a heating tape controlled by a voltage regulator.

The oxidation products are cooled and condensed in two glass condensers in series and collected in a glass flask. Cooling is achieved by tap water. The temperature was measured in various locations along the system by thermocouples of type J.

While the benzoic acid and steam were heated, the reaction zone was also heated up to the desired temperature in hot airflow. After the benzoic acid is vaporized, in the round bottom flask, air was then bypassed into the flask to carry over amount of the acid; this amount depends on time of vaporization. Steam, in a specified amount, was then introduced and mixed with the flow of air-benzoic acid in the entrance of the preheating section.

The oxidation products of unreacted benzoic acid, benzene, and other products were collected in a cooled trap and analyzed by gas chromatography using thermal conductivity detector.

### Characterization

The specific surface area and the pore distribution of each catalyst were measured by the BET technique with a Shimadzu ASAP2000. X-ray diffraction (XRD) patterns were obtained using nickel filtered Cuk□ radiation with a Riga Ku RU-300diffractometer.The measurement was carried out in Al-Raya Company.

## RESULTS AND DISCUSSION

### Influence of Catalyst Composition

It was found that $Fe_2O_3$ and NiO catalysts gave low conversion levels at reaction temperature of 300°C; however, NiO catalyst showed high phenol selectivity (above 40%) at reaction temperature of 400°C. It was obvious that $Fe_2O_3$ catalyst exhibits higher conversion and lower phenol selectivity compared with those of NiO catalyst. As indicated in table (1), a combination of these oxides at different proportion of NiO-$Fe_2O_3$ combined catalysts prepared by co-precipitation was examined to show their effect on the conversion and phenol selectivity. As indicated in table (2), it was found that a combination of NiO and $Fe_2O_3$ be very effective to obtain higher conversion and maintaining high phenol selectivity compared with those of mono oxide catalysts. The results suggesting that the combination of NiO and $Fe_2O_3$ (70 wt.% NiO – 30 wt.% $Fe_2O_3$) gave higher conversion and phenol selectivity.

On the other hand, a NiO-$Fe_2O_3$ catalyst prepared by co-precipitation consisting of $NiFe_2O_4$ phase, and with atomic ratio of Ni to Fe of 0.5 gave poor phenol selectivity and higher conversion of benzoic acid compared with the combination of NiO and $Fe_2O_3$ (70 wt.% NiO - 30 wt.% $Fe_2O_3$).

Several catalyst consisting of NiO, $Fe_2O_3$ and $NiFe_2O_4$ with different Ni/Fe were prepared and catalytic activities were examined in order to speculate on the active species. The catalyst with the atomic ratio of Ni to Fe 1.0, namely equimolar quantities of NiO and $NiFe_2O_4$, exhibited optimum phenol selectivity and benzoic acid conversion. On the other hand, the Ni-rich catalysts gave low conversions, while the Fe-rich catalysts showed low selectivities to phenol as indicated in table (3).

Results indicated that single-phase $NiFe_2O_3$ is insufficient for the formation of active species for phenol production. Besides, the catalyst with an atomic ratio of Ni to Fe of 0.25, namely $Fe_2O_3$ and $NiFe_2O_4$, exhibited low phenol selectivity. On the contrary, the catalysts that consist of NiO and $NiFe_2O_4$ gave relatively high phenol selectivity, indicating that two kinds of these oxides are necessary with the atomic ratio of Ni to Fe of 1.0, i.e. exhibited good catalyst performance. These results suggest that the active form of the catalyst is not $NiFe_2O_4$ or $Fe_2O_3$ but probably NiO dispersed in $NiFe_2O_4$.

### Influence of Catalyst Surface Area

In the precipitation catalyst, it was revealed that the calcination temperature greatly affects the catalytic activity. Optimum phenol selectivity was obtained at calcination temperature of 800°C while the selectivity of benzene increased below 600°C and over 1000°C due to rapid rise in benzene formation. The results obtained are tabulated in table (4).

The conversion decreases markedly with a decrease in surface area below 6.1 m2/g. On the other hand, the phenol selectivity decreases gradually with increasing surface areas. Good catalytic performance was obtained at a calcintion temperature of 800°C (1073°K), exhibiting 75% in phenol selectivity with 82% in benzoic acid conversion. Rapid drop in conversion at a calcination temperature of 1000°C (1273°K) is obviously due to the decrease of surface area. However, the catalyst calcined at 600 and 700°C (873 and 973°K) showed lower phenol selectivity normalized by surface area compared with that of catalyst calcined at 800°C (1073°K).

It is difficult to explain this result from the effect of catalyst surface area. The drastic influence of calcination temperature on activities of precipitated catalysts might be attributed to the difference of both physical structures.

### Influence of reaction temperature

The result obtained here, are tabulated in table (5). These results clearly demonstrate that increasing temperature up to 400°C causes the benzoic acid conversion, phenol selectivity and yield to increase. Beyond this temperature the phenol selectivity and yield decreases. This decreases and increase in phenol and benzene selectivity respectively was due to the enhanced decomposition of phenyl benzoate to benzene and carbon dioxide.

### Influence of Oxygen Ratio

Figures 1 and 2 shows the effect of the O2/benzoic acid molar ratio on catalytic activities. With increasing oxygen molar ratio, benzoic acid conversion increased linearly, while phenol selectivity exhibited a gradual decrease. Benzene selectivity seemed to be almost constant below an oxygen molar ratio of 2.1 (for air this ratio is 10). Complete combustion products appeared to increase above an oxygen molar ratio of 1.68 (for air this ratio is 8). An oxygen molar ratio of about 1.68 seems to be appropriate to achieve a highest yield of phenol over the nickel-iron oxide catalyst.

### Influence of steam ratio

The activity of the catalyst is strongly influenced by the presence of water vapor in the reactant stream. It is desired to obtain phenol as the main product, so the steam is advantageously introduced into the reaction zone so as to hydrolyze in-situ any esters of phenolic compounds and benzoic acid that may primarily be formed. The rate of hydrolysis depends on the amount of steam introduced and the reaction conditions including, for instance, the reaction temperature. Preferably, the molecular ratio of steam to benzoic acid in the total gaseous feed is about 25.

Fig. 3 and 4 shows the effect of the steam/benzoic acid molar ratio on the catalyst activities. Benzoic acid conversion and benzene selectivity appeared to be almost constant above a steam/benzoic acid molar ratio of 30. While the phenol selectivity showed rapid decrease below a steam/benzoic acid molar ratio of 20 due to the formation of phenyl benzoate. It is found that steam/benzoic acid molar ratio of more than 20 were necessary to have the hydrolytic cleavages of phenyl benzoate proceed completely and maintain high phenol selectivity.

### Influence of Space Velocity

The results obtained are tabulated in table (6). The benzoic acid conversion decreased with a rise in space velocity. It is noteworthy that the increase in space velocity affects the selectivities to each of the products, i.e. benzene selectivity increase, while the best value of phenol selectivity is about 3030 h-1. Below this space velocity, the selectivity decreases due to short residence time. Maximum phenol yield appeared to be at a space velocity of 3030 h-1 at the reaction temperature of 400°C.

## CONCLUSIONS

As a result of this work, it was found that NiO and Fe2O3 showed catalytic activity for the vapor phase oxidation of benzoic acid to phenol in the temperature range above 350°C. The combination of NiO and Fe2O3 is also found to exhibit high conversion maintaining high phenol selectivity. Especially, co-precipitation method is effective for the enhancement of catalyst activity. The catalyst with Ni/Fe atomic ratio of 1 and with surface area of 6.1 m2/gm exhibits excellent activity for the vapor phase oxidation of benzoic acid to phenol.

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Table (1) Results of experimental runs for catalyst composition effect*

| Catalyst composition | Reaction temperature (°C) | Conversion of BzOH (%) | Selectivity (%) | | | | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | | Phenol | Benzene | Phenyl benzene | Other products | |
| $Fe_2O_3$ | 300 | 15.8 | 26.1 | 50.9 | 2.1 | 20.9 | 4.1 |
| | 350 | 20.2 | 29.3 | 52.3 | 1.7 | 16.7 | 5.9 |
| | 400 | 32.6 | 34.2 | 59.1 | - | 6.7 | 11.1 |
| | 450 | 45.7 | 20.5 | 64.3 | - | 15.2 | 9.4 |
| NiO | 300 | 8.6 | 35.1 | 35.2 | 4.2 | 25.5 | 3 |
| | 350 | 11.3 | 41.9 | 37.5 | 3.2 | 17.4 | 4.7 |
| | 400 | 19.2 | 48.2 | 40.6 | - | 11.2 | 9.3 |
| | 450 | 30.6 | 32.6 | 50 | - | 17.4 | 10 |

* *Molar ratio of benzoic acid/air/steam ratio=1/10/30, calcination temperature = 800°C, space velocity = 3182* $h^{-1}$

Table (2) Results of experimental runs for catalyst composition effect*

| Catalyst composition | Space velocity ($h^{-1}$) | Conversion of BzOH (%) | Selectivity (%) | | | | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | | Phenol | Benzene | Phenyl benzene | Other products | |
| 70 wt% NiO<br>30 wt% $Fe_2O_3$ | 3354 | 58 | 55 | 55 | - | 15 | 31.9 |
| 50 wt% NiO<br>50 wt% $Fe_2O_3$ | 3237 | 51 | 49 | 35 | - | 16 | 25 |
| 30 wt% NiO<br>70 wt% $Fe_2O_3$ | 3182 | 48 | 47 | 40 | - | 13 | 22.6 |
| $NiFe_2O_4$<br>(Ni/Fe=0.5) | 3182 | 79 | 30 | 58 | - | 12 | 23.7 |

* *Molar ratio of benzoic acid/air/steam ratio = 1/10/30, reaction temperature = 400°C (673°K)*

Table (3) Results of experimental runs for catalyst composition effect*

| Catalyst | | | Conversion BzOH (%) | Selectivity (%) | | | Yield (%) |
|---|---|---|---|---|---|---|---|
| Ni/Fe atomic ratio | $NiO/NiFe_2O_4/Fe_2O_3$ | Surface area ($m^2/g$) | | Phenol | Benzene | Other products | |
| 0.25 | 0/1/1 | 6.2 | 60 | 40 | 45 | 15 | 24 |
| 0.33 | 0/1/2 | 8.1 | 68 | 31 | 52 | 17 | 21.1 |
| 0.75 | 0.5/1/0 | 7.8 | 72 | 66 | 20 | 14 | 47.5 |
| 1.0 | 1/1/0 | 6.1 | 82 | 75 | 15 | 10 | 61.5 |
| 1.63 | 2.3/1/0 | 3.8 | 76 | 70.5 | 13 | 16.5 | 53.6 |
| 2.0 | 3/1/0 | 2.7 | 59 | 59 | 16 | 15 | 40.7 |

**Molar ratio of benzoic acid/air/steam ratio = 1/10/30, reaction temperature = 400°C (673°K), space velocity = 3182 $h^{-1}$, calcination temperature = 800°C (1073°K)*

Table (4) Results of experimental runs for catalyst surface area effect*

| Calcination temperature (°C) | Surface area ($m^2/g$) | Conversion BzOH (%) | Selectivity (%) | | | Yield (%) |
|---|---|---|---|---|---|---|
| | | | Phenol | Benzene | Other products | |
| 500 | 24 | 88 | 40.1 | 43.1 | 16.8 | 35.3 |
| 600 | 23 | 87 | 48.4 | 40 | 11.6 | 42.1 |
| 700 | 18 | 85 | 54.1 | 28 | 17.9 | 46 |
| 800 | 6.1 | 82 | 75 | 15 | 10 | 61.5 |
| 1000 | 0.2 | 10.3 | 43 | 50 | 7 | 4.4 |

**Catalyst used $Ni/NiFe_2O_4$ with Ni/Fe =1, Molar ratio of benzoic acid/air/steam ratio = 1/10/30, reaction temperature = 400°C (623°K), space velocity = 3182$h^{-1}$*

Table (5) Results of experimental runs for reaction temperature effect*

| Reaction temperature (°C) | Conversion of BzOH (%) | Selectivity | | | | Yield (%) |
|---|---|---|---|---|---|---|
| | | Phenol | Benzene | Phenyl benzoate | Other products | |
| 300 | 65 | 64 | 10 | 12 | 14 | 41.6 |
| 350 | 72 | 69 | 12 | 8 | 11 | 49.7 |
| 400 | 82 | 75 | 15 | - | 10 | 61.5 |
| 450 | 85 | 50 | 35 | - | 15 | 42.5 |

**The catalyst used $NiO/NiFe_2O_4$ with Ni/Fe=1 and calcination temperature, surface area = 6.1 $m^2/g$, molar ratio of benzoic acid/air/steam ratio=1/10/30, space velocity = 3182 $h^{-1}$*

Table (6) Results of experimental runs for space velocity effect*

| Catalyst weight (g) | Space velocity ($h^{-1}$) | Conversion of BzOH (%) | Selectivity (%) | | | | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | | Phenol | Benzene | Phenyl benzene | Other products | |
| 75 | 4028 | 61 | 62 | 25 | 5 | 8 | 37.5 |
| 100 | 3030 | 80 | 82 | 13 | - | 5 | 65.6 |
| 125 | 2412 | 86 | 72 | 17 | - | 11 | 61.9 |
| 150 | 2014 | 89 | 65 | 19 | - | 16 | 57.9 |

** The catalyst used $NiO/NiFe_2O_4$ with Ni/Fe=1, calcination temperature=800°C (1073°K), surface area=6.1 $m^2/g$, reaction temperature=400°C (623°K), molar ratio of benzoic acid/air/steamr=1/8/30.*

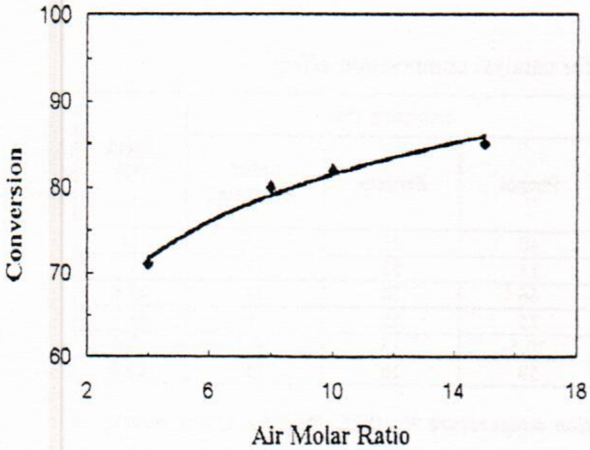

Fig. (1) Effect of air molar ratio on the conversion of benzoic acid (the catalyst used is NiO/NiFe$_2$O$_4$ with Ni/Fe=1, calcination temperature=800°C, surface area = 6.1 m$^2$/g, reaction temperature = 400°C (673°K), molar ratio of benzoic acid to steam=1/30)

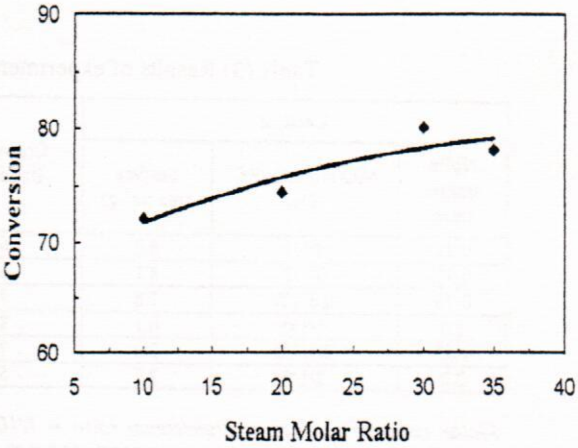

Fig. (3) Effect of steam molar ratio on the conversion of benzoic acid. (the catalyst used is NiO/NiFe$_2$O$_4$ with Ni/Fe=1, calcination temperature=800°C, surface area = 6.1 m$^2$/g, reaction temperature = 400°C (673°K), molar ratio of benzoic acid to air=1/8)

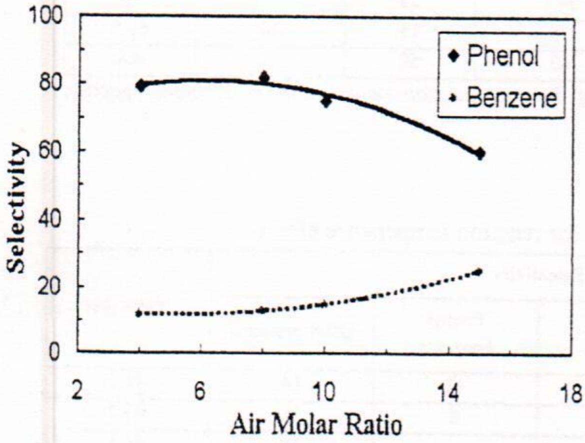

Fig. (2) Effect of air molar ratio on selectivity of phenol and benzene. (the catalyst used is NiO/NiFe$_2$O$_4$ with Ni/Fe=1, calcination temperature=800°C, surface area = 6.1 m$^2$/g, reaction temperature = 400°C (673°K), molar ratio of benzoic acid to steam=1/30)

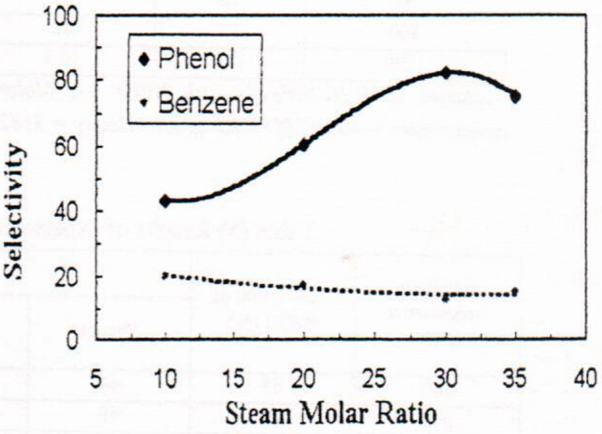

Fig. (4) Effect of steam molar ratio on selctivity of phenol and benzene. (the catalyst used is NiO/NiFe$_2$O$_4$ with Ni/Fe=1, calcination temperature=800°C, surface area = 6.1 m$^2$/g, reaction temperature = 400°C (673°K), molar ratio of benzoic acid to air=1/8)