

IMPROVING THE ACTIVITY OF NiO-NiFe₂O₄ CATALYST BY Na₂O FOR PHENOL SYNTHESIS

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ABSTRACT

An NiO-NiFe₂O₄-Na₂O catalyst achieved an extremely high yield of phenol, while maintaining a high phenol selectivity, as compared with that of a conventional CuO catalyst for the vapor phase oxidation of benzoic acid. The addition of Na₂O to NiO-NiFe₂O₄ catalyst was found to be very effective in increasing the yield of phenol, while maintaining a high phenol selectivity. The effect of temperature, oxygen ratio, steam ratio, and space velocity on the catalyst performance were examined in order to optimize the phenol selectivity and yield of phenol.

INTRODUCTION

The oxidation of toluene to phenol via benzoic acid is one of the conventional methods for commercial production of phenol. In this process, toluene is first oxidized to benzoic acid in the liquid phase using a cobalt-manganese catalyst, and then the benzoic acid is oxidized to phenol using copper catalyst in the liquid phase. However, a poor phenol yield and tar formation have been reported for the latter reaction using a Cu-based catalyst in the liquid phase and these problems still remain unsolved^[1-9]. Hence, the development of catalysts which yield phenol from benzoic acid in high efficiency has been pursued for a long time. From an industrial point of view, the vapor phase method for the oxidation of benzoic acid to phenol is considered to be a very attractive because of its simplicity with respect to product purification and catalyst regeneration. Considerable research has also been performed on CuO and NiO-Fe₂O₃ catalysts in the vapor phase oxidation of benzoic acid to form phenol selectivity^[10-13].

In the present work, we found that modification of the NiO-NiFe₂O₄ catalyst with Na₂O enhances the yield of phenol considerably. In addition, we examined in detail the effect of the reaction conditions on catalytic activity.

EXPERIMENTAL WORK

Catalyst

Ni-Fe complex oxide catalysts were prepared by coprecipitation using aqueous solution of

nickel nitrite, iron nitrite, and sodium hydroxide. The precipitates obtained were washed with pure water until they become free from sodium and then dried in air at a temperature of 110°C for 24 hr. After calcinations in air at temperature of 800°C for 3 hr, the catalysts were pulverized to particles in the range of 20-40 mesh. Modification with Na₂O was performed using impregnation method with water solution of sodium carbonate (5g in 30 ml water). The impregnated catalysts were calcined again at 500°C for 3 hr.

Properties of The Prepared Catalyst
(NiO-NiFe₂O₄-Na₂O)

Property	Value
Apparent porosity %	0.24
Pore volume ml/g	0.18
Particle Density g/ml	1.9
Packed bed Density g/ml	0.9
Packed bed Voidage	0.6
Bulk crushing strength Kg/cm ²	5
Loss on attrition wt. %	1
Normal size	20-40 mesh
Surface area m ² /g	6

Apparatus and Procedure

The reaction was carried out using a conventional flow reactor at atmospheric pressure. The reactor was made of a QVF tube with an inner diameter of 2.54 cm and a length of 70 cm. The experiments were carried out in the presence of steam. An amount of 100 g of the catalyst was used and the reaction temperature

was measured by a thermocouple placed in a thermo well with the catalyst bed.

While the benzoic acid and steam were heated, the reaction zone was also heated up to the desired temperature in hot air flow. After benzoic acid is vaporized in the round bottom flask, air was then passed 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 phenol, unreacted benzoic acid, benzene, and other products were collected in a cold trap and analyzed by gas chromatography using conductivity detector.

RESULTS AND DISCUSSION

Effect of Na₂O on the NiO-NiFe₂O₄ catalyst

As shown in Table (1), NiO-NiFe₂O₄ catalyst showed a 75% phenol selectivity with 82% benzoic acid conversion under a space velocity of 2520 hr⁻¹, however further improvement seems to

be required for the industrial application of this process.

We found that the catalyst activity was greatly enhanced by the addition of alkali or alkaline earth metal oxides to the NiO-NiFe₂O₄ catalyst. As shown in Table (1), Na₂O promoted catalyst showed excellent catalytic performance, 90% phenol selectivity with 92% benzoic acid conversion. The initial stage of the reaction would be an adsorption of benzoic acid on the base component, probably NaOH formed from Na₂O or NaNiO₂ in the presence of steam. After the formation of sodium benzoate, it is transferred to benzoyl salicylic acid which is an intermediate for phenol formation. The enhancement of the conversion by the additives can probably be attributed to the acceleration of the adsorption of benzoic acid on the catalyst surface to form sodium benzoate. On the other hand, the increase of phenol selectivity is presumed to be caused by the formation of sodium benzoate which is more stable than benzoic acid from a thermochemical point of view. It is speculated that the decomposition of benzoic acid to benzene and carbon dioxide over the NiO-NiFe₂O₄-Na₂O Catalyst inhibited due to the stability of sodium benzoate, which leads to the increase in phenol selectivity.

Table (1) Effect of Na₂O on conversion and selectivity^a

Additive ^b	Reaction temp. (°C)	Conversion (%)	Selectivity ^c		
			Phenol	Benzene	Other
None	350	72	69	12	19
None	400	82	75	15	10
None	450	85	50	35	15
Na ₂ O	350	85	82	5	13
Na ₂ O	400	92	90	6	4
Na ₂ O	450	95	71	20	9

^a Catalyst: 47 wt.% NiO-51 wt.% NiFe₂O₄-2 wt.% additive; calcined at 800°C; reaction conditions: benzoic acid/air/steam=1/12/30; space velocity=2520 hr⁻¹.

^b Impregnated with an aqueous solution of sodium carbonates

^c Selectivity is calculated on the basis of moles benzoic acid converted.

Effect of Na₂O content on catalyst activities

Table (2) shows the effect of Na₂O content on catalytic activity. An Na₂O content of 2 wt.% was found to be very effective for optimal catalytic activity both as regards phenol selectivity and conversion. On the other whole, the conversion and phenol selectivity decreased and benzene selectivity increased rapidly with increasing Na₂O

content. The results suggest that the decrease in conversion with increasing Na₂O content was caused by the accumulation of sodium benzoate, covering the active sites on the catalyst surface. It can also be presumed that the decrease in phenol selectivity and the increase in benzene selectivity with increasing Na₂O content result from the decomposition of sodium benzoate accumulated over a period of time on the catalyst surface.

Table (2) Effect of Na₂O content on catalytic activities^a

Na ₂ O content ^b (wt.%)	Conversion (%)	Selectivity ^c		
		Phenol	Benzene	Other
0.5	75	82	10	8
1.0	80	85	7	8
2.0	92	90	6	4
5.0	50	45	50	5

^a Catalyst Fe/Ni ratio = 1 (atomic ratio); prepared by coprecipitation; reaction conditions: benzoic acid/air/steam = 1/12/30 (molar ratio); space velocity 2520 hr⁻¹; reaction temperature = 400°C.

^b Impregnated with an aqueous solution of metal nitrite or carbonates

^c Selectivity is calculated on the basis of moles benzoic acid converted.

Effect of operating conditions on catalyst activity

Fig. (1) exhibits the effect of reaction temperature on catalytic activities. A gradual decrease in phenol selectivity and increase in benzene selectivity were observed with increasing reaction temperature. The decrease in phenol selectivity and increase in benzene selectivity with a rise in reaction temperature was probably due to the enhanced decomposition of sodium benzoate to benzene and carbon dioxide.

Fig. (2) exhibits the effect of the O₂/benzoic acid molar ratio on catalytic activities. With increasing oxygen molar ratio, benzoic acid conversion increase linearly, while phenol selectivity exhibited a gradual decrease. Benzene selectivity seemed to be almost constant below an oxygen molar ratio of 2.49. Complete combustion products appeared to increase above an oxygen molar ratio of 2.52. An oxygen molar ratio of about 2.52 seems to be appropriate to achieve a high yield of phenol over the NiO-NiFe₂O₄-Na₂O catalyst.

Fig. (3) 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 a rapid decrease below a steam/benzoic acid ratio of 20, because of the formation of phenyle benzoate. It was found that a steam/benzoic acid molar ratio of more than 20 was necessary to have the hydrolytic clearages of phenyle benzoate proceed completely and to maintain high phenol selectivity.

Fig. (4) exhibits the effect of the space velocity on catalyst performance. The

benzoic acid conversion decreased with a rise in space velocity. It is noteworthy that the increase in space velocity hardly affects the selectivity to each of the products. The maximum yield of phenol appeared to be at space velocity of around 2520 hr⁻¹ at a reaction temperature of 400°C.

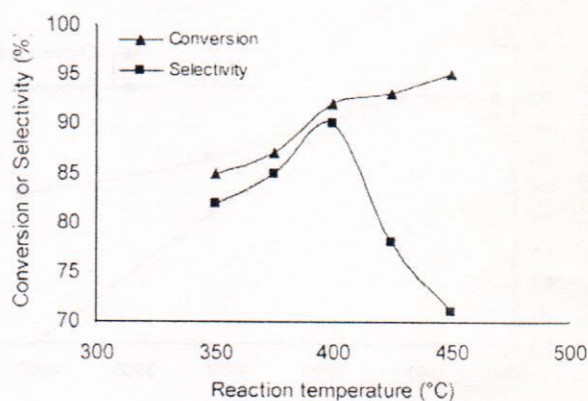


Fig. 1 Effect of reaction temperature on catalyst activity; catalyst: 47 wt.% NiO-51 wt.% NiFe₂O₄-2 wt.% Na₂O; feed gas: acid/air/steam (molar ratio)=1/12/30; space velocity =2520 hr⁻¹.

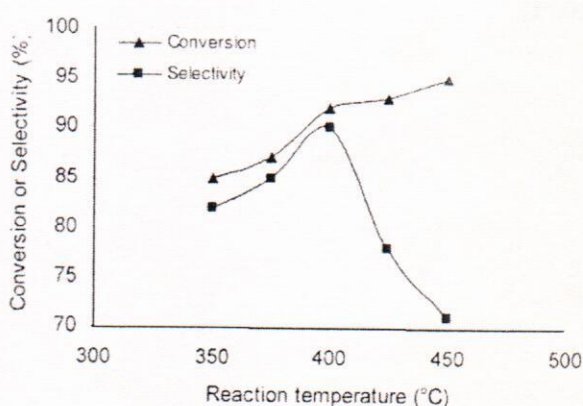


Fig. 2 Effect of O₂/benzoic acid molar ratio on catalyst activity; catalyst: 47 wt.% NiO-51 wt.% NiFe₂O₄-2 wt.% Na₂O; feed gas: benzoic acid/air/steam (molar ratio)=1/x/30; Reaction temperature 400°C; space velocity 2520 hr⁻¹.

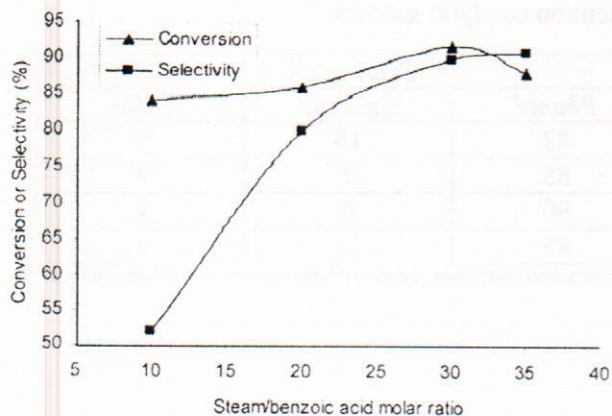


Fig. 3 Effect of steam/benzoic acid molar ratio on catalyst activity; Catalyst: 47 wt.% NiO-51 wt.% NiFe₂O₄-2 wt.% Na₂O; feed gas: benzoic acid/air/steam (molar ratio)=1/12/x; space velocity =2520 hr⁻¹; reaction temperature = 400°C.

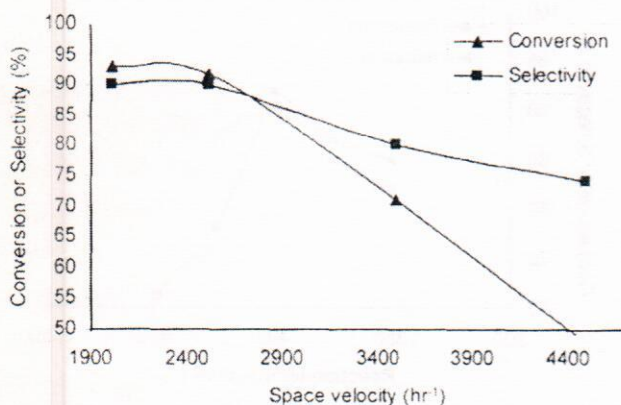


Fig. 4 Effect of space velocity on catalyst activity. Catalyst: 47 wt.% NiO-51 wt.% NiFe₂O₄-2 wt.% Na₂O; feed gas: benzoic acid/air/steam (molar ratio)=1/12/30; space velocity =2520 hr⁻¹; reaction temperature = 400°C.

CONCLUSIONS

The addition of Na₂O to NiO-NiFe₂O₄ complex oxide was found to be very effective to enhance the yield of phenol, while maintaining a high phenol selectivity. It is proved that the content of Na₂O on the catalyst affects the catalyst performance greatly. The reaction ratio of the sodium benzoate formation on the surface is assumed to be a crucial factor for the phenol selectivity.

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