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Vapor Phase Oxidation of Benzoic Acid to Phenol over a Novel Catalyst System Consisting of NiO and $NiFe_2O_4$

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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. The homogeneous distribution profile of NiO and $NiFe_2O_4$ on the surface and in the bulk of the catalyst is essential for the optimization of phenol formation.

INTRODUCTION

Phenol is one of the most important starting materials for various chemical products, such as phenol resin, bisphenol A, aniline, and some agricultural chemicals. Although a number of methods for phenol syntheses have been proposed, the cumene process 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. In addition, acetone, which is also a commercially important chemical, is coproduced with phenol in the process. However, a problem has arisen: The demand for acetone has decreased recently, while the demand for phenol has enormously increased. The imbalance of demand between phenol and acetone have 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 oxidized to phenol using a copper catalyst. According to some literature and patents, the copper catalysts for the latter reaction have problems such as low yield of phenol, tar formation, and catalyst deactivation (1–15). In spite of the attempts to improve the copper-based catalyst, these problems remain unsolved at present, necessitating development of a more efficient catalyst. In this paper, we propose an entirely novel catalyst that consists of nickel and iron oxides, which throws a new light upon the development of the catalyst for the vapor phase oxidation of benzoic acid to phenol (16–18).

METHODS

Catalysts. The titania-supported catalysts were prepared by impregnating a commercially available granular anatase-type titanium oxide (Merk, particle size 20–40 mesh) with aqueous solutions of metal nitrates, followed by drying at 100°C and then calcining in air at 500°C for 3 h. The precipitation method with aqueous solutions of metal nitrates and sodium hydroxide was also used for the preparation of NiO, Fe_2O_3, and NiO–Fe_2O_3 combined catalysts. The precipitates obtained were washed with pure water until they became free from sodium and then dried in air at a temperature of 110°C for 24 h. After calcination in air at a temperature of 400–800°C for 3 h, the catalysts were crushed to particles in the range of 20–40 mesh.

Apparatus and procedure. A continuous flow-type reaction apparatus with a fixed catalyst bed was used at atmospheric pressure. The reactor was made of a quartz tube with an inner diameter of 20 mm and a length of 500 mm. The experiments were carried out in the presence of steam. Molten benzoic acid was supplied to the reactor with a hot steel syringe which was heated to 130°C. The organic products were collected as follows: initially the product gas was bubbled through liquid acetone at about 0°C and then collected products that were trapped again by a dry ice–methanol trap system at about −70°C. The liquid acetone and the collected products were mixed and were analyzed by a gas chromatograph using an on-line thermal conductivity detector. Phenol, benzene, CO, CO_2, and trace amounts of biphenyl and phenyl benzoate were detected upon analysis. Product selectivities were calculated on the basis of benzoic acid converted. CO and CO_2 calculated for CO + CO_2 selectivity was intended

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TABLE 1

Results of Blank Test and Quantitative Analyses on the Stainless Steel Surface of Reactors[a]

Reactor number	Conversion (%)	Selectivity[b] (%)			Surface composition of reactor wall[c] (atom%)					
		Phenol	Benzene	CO, CO_2	Fe	Ni	Cr	Mo	C	O
1[d]	38	43	15	32	6.5	tr	1.3	0.3	39.7	53.2
2[d]	58	66	15	16	5.1	tr	0.3	0.5	59.4	34.8
3[e]	0.1	0	0	100	—	—	–	—	—	—

[a] Reaction conditions: benzoic acid/air/steam/N_2 = 1/10/50/15 (molar ratio); benzoic acid = 5.00×10^{-5} mol/min; reaction temperature = 500°C. Blank test was performed without packing any catalysts in the stainless steel or quartz reactors.

[b] Calculated on the basis of moles benzoic acid converted.

[c] Measured by XPS analyses.

[d] Made of stainless steel.

[e] Made of quartz.

to be generated from complete combustion of benzoic acid. Therefore, CO_2 generated through oxidation to phenol ($C_6H_5COOH + 1/2O_2 \rightarrow C_6H_5OH + \underline{CO_2}$) was not included in the CO + CO_2 selectivity.

Characterization. The specific surface area and the pore distribution of each catalyst was measured by the BET technique with a Shimadzu ASAP2000. X-ray diffraction (XRD) patterns were obtained using nickel filtered Cu*Kα* radiation with a Rigaku Ru-300 diffractiometer. Electron probe microanalysis (EPMA) was performed using a Shimadzu EMX-SM7. The electron gun was operated at 15 kV and the transitions chosen for this study were *Kα* for Fe and Ni. X-ray photoelectron spectroscopy (XPS) analyses were performed by an SSI SSX-100 instrument with Al*Kα* X-ray radiation. Quantitative determinations were made by correcting the ratios of the peak areas ($Fe2p_{3/2}$, $Ni2p_{3/2}$) using the instrumental sensitivities for the pure oxides.

RESULTS

We first discovered the activities of NiO and Fe_2O_3 from the result that a small amount of phenol was produced from benzoic acid without packing any catalysts into the stainless steel reactor as shown in Table 1. It is obvious that the surface of the reactor wall catalyzes the oxidation of benzoic acid to phenol.

Since the stainless steel reactor consists of Fe, Ni, Cr, and Mo, the catalytic activity of these oxides impregnated in titanium oxide were examined, respectively, as shown in Table 2. Among them, NiO/TiO_2 and Fe_2O_3/TiO_2 exhibited the catalytic activities for phenol production in the temperature range of 350 to 450°C. It was also found that catalysts prepared by precipitation gave higher conversion than the titania-supported NiO or Fe_2O_3 catalysts. Both in impregnated catalysts and in precipitation catalysts, the combination of NiO and Fe_2O_3 was found to be very effective to obtain higher conversion maintaining high phenol selectivity compared with those of monoxide catalysts. The possible pathways for phenol production over Ni–Fe catalysts are shown in Fig. 1 (12–15).

In the precipitation catalyst, it was revealed that the calcination temperature greatly affects the catalytic activity as shown in Table 3. An optimum phenol selectivity was obtained at the calcination temperature of 800°C, while the selectivity to benzene increased below 600°C and over 1000°C due to a rapid rise in benzene formation.

In order to confirm the catalyst structure, the characterization studies were performed using XRD. As exhibited in Fig. 2, it was proved that the catalyst calcined at 800°C consists of two kinds of oxides, namely NiO and $NiFe_2O_4$.

Several catalysts consisting of different Ni/Fe atomic ratio were prepared and catalytic activities were examined in order to speculate the active species as presented in Table 4. The structure of oxides contained in the catalysts were identified from XRD analyses, indicating that the phases in the catalysts depended on the Ni/Fe composition. It was shown that $NiFe_2O_4$ is formed in preference to NiO or Fe_2O_3 under the preparation conditions. The catalyst with the atomic ratio of Ni to Fe of 1, namely equimolar quantities of NiO and $NiFe_2O_4$, exhibited the optimum phenol selectivity and the optimum benzoic acid conversion. On the other hand, the Ni-rich catalysts gave low conversions, while the Fe-rich catalysts showed low selectivities to phenol.

Physical analysis was performed for the catalyst which exhibited the optimum activity for phenol formation, that is, the catalyst with the atomic ratio of Ni to Fe of 1. The pore diameter distribution of the catalyst is exhibited in Fig. 3. Figure 4 shows the conversion and the phenol selectivities plotted against the surface areas of the cata-

TABLE 2

Activities of Various Catalysts for the Vapor Phase Oxidation of Benzoic Acid[a]

Catalyst[b]	Temperature (°C)	Space velocity (h^{-1})	Conversion (%)	Selectivity (%)[c]		
				Phenol	Benzene	$CO + CO_2$
10 wt%NiO/TiO_2[d]	350	3200	1.7	70.3	21.3	0.1
10 wt%NiO/TiO_2[d]	400	3200	6.3	72.3	12.4	10.5
10 wt%NiO/TiO_2[d]	450	3200	17.6	56.8	37.1	1.1
10 wt%Fe_2O_3/TiO_a[d]	350	3200	5.2	49.1	38.4	1.0
10 wt%Fe_2O_3/TiO_2[d]	400	3200	17.6	41.3	46.5	12.2
10 wt%Fe_2O_3/TiO_2[d]	450	3200	32.7	18.5	60.9	10.8
5 wt%MoO_3/TiO_2[d]	400	3200	1.9	2.0	33.4	64.0
10 wt%Cr_2O_3/TiO_2[d]	400	3200	tr	tr	tr	tr
5 wt%CuO/TiO_2[d]	300	3200	81.8	8.5	84.3	3.0
5 wt%CuO/TiO_2[d]	400	3200	96.9	3.0	90.5	4.9
5 wt%NiO–5 wt%Fe_2O_3/TiO_2[d]	400	2060	13.7	82.0	14.7	3.9
Fe_2O_3[e]	370	8800	33.7	52.2	45.2	2.1
NiO[e]	350	10570	20.5	16.7	8.5	74.5
50 wt%Fe_2O_3–50 wt%NiO[e]	370	5280	49.6	63.0	28.5	7.5

[a] Reaction conditions: benzoic acid/air/steam/N_2 = 1/2/30/10 (molar ratio); benzoic acid = 2.74 × 10^{-4} mol/min; catalyst weight = 4.0 g.
[b] Calcination temperature = 500°C.
[c] Calculated on the basis of moles benzoic acid converted.
[d] Prepared by impregnation.
[e] Prepared by precipitation.

lysts calcined at 800°C. The surface area is controlled by the calcination time (19–22). Conversion decreases markedly with a decrease in the surface area below 5 m^2/g. On the other hand, the phenol selectivities decrease gradually with increasing surface areas. Figure 5 exhibits the results of EPMA. The cylindrical catalyst (Ni/Fe = 1) was analyzed along the dotted line in the figure. Evidently the catalyst has a very homogeneous profile.

The composition analyses were performed by EPMA and XPS in order to investigate the relation of the component between the surface and the bulk. The linear correlation was obtained as shown in Fig. 6.

Figure 7 exhibits the XPS spectra of the $Ni2p_{3/2}$ level of NiO, $NiFe_2O_4$, and the catalyst (Ni/Fe = 1). The signal of the catalyst shown in the middle tier appears to be of a shape and width between those of NiO and $NiFe_2O_4$ (23–27).

DISCUSSION

Contrary to the fact that CuO catalyst has been regarded as the only active species for oxidation of benzoic acid to phenol, it was discovered that NiO/TiO_2 and Fe_2O_3/TiO_2 exhibited the catalytic activities for the reaction as

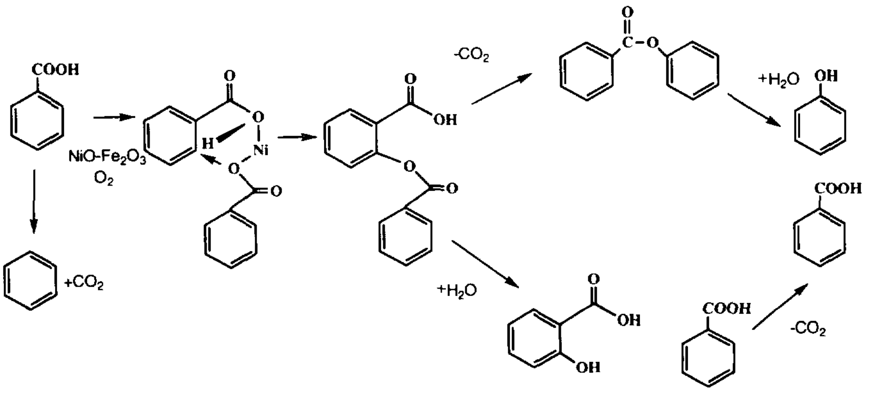


FIG. 1. Possible pathways for phenol production over Ni–Fe catalysts.

TABLE 3

Effect of Calcination Temperature on Catalytic Activity[a]

Calcination temperature (°C)	Surface area[b] (m^2/g)	Conversion (%)	Selectivity (%)[c] Phenol	Benzene	CO + CO_2	Rate of phenol formation ($\times 10^{-5}$ mol/m^2 h)
400	25.0	—[d]	—[d]	—[d]	—[d]	—[d]
600	23.7	94	51	44	3	0.73
700	18.1	76	53	14	30	0.80
800	6.1	100	93	5	1	5.51
1000	0.1	0.2	43	50	6	0.31

[a] Catalysts: NiO–Fe_2O_3 (Ni/Fe atomic ratio = 1); prepared by coprecipitation. Reaction conditions: benzoic acid/air/stream/N_2 = 1/10/50/15 (molar ratio); catalyst weight = 20.0 g (7.7 ml); space velocity = 1600 h^{-1}; reaction temperature = 400°C.

[b] The values are obtained by BET technique with nitrogen adsorption.

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

[d] Too much exothermic reaction proceeded to maintain a steady temperature.

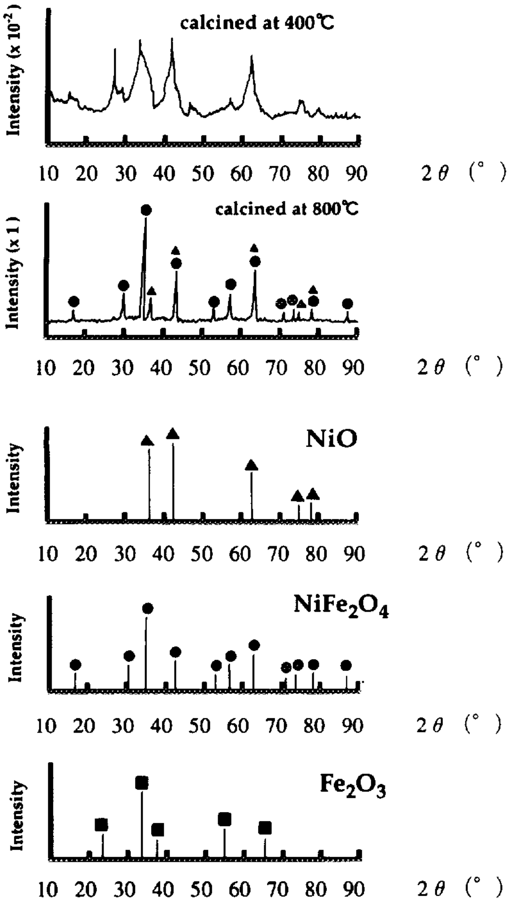


FIG. 2. XRD patterns of the catalysts and reference patterns of metal oxides.

shown in Table 2. They gave low conversion levels at a reaction temperature of 350°C; however, NiO/TiO_2 showed high phenol selectivity above 70%. It was obvious that Fe_2O_3/TiO_2 exhibits higher conversion and lower phenol selectivity compared with those of NiO/TiO_2. In comparison to these catalysts, CuO/TiO_2 catalyst showed higher conversion at 400°C, but lower phenol selectivity due to a large amount of benzene being formed. The results suggest that the oxidation potential of NiO and Fe_2O_3 is lower than that of CuO. However, the reaction over Ni or Fe oxides is basically presumed to proceed on the similar mechanism as over CuO (12–15). Some possible intermediates are illustrated in Fig. 1. Salicyclic acid is considered to be an intermediate to phenol formation and hydrogen in ortho position of carboxylic group is presumed to be substituted by hydroxyl group. A NiO–Fe_2O_3/TiO_2 catalyst gave higher phenol selectivity, suggesting that the combination of NiO and Fe_2O_3 was effective for the selective formation of phenol. Although NiO and Fe_2O_3 prepared by precipitation exhibits higher conversion than NiO/TiO_2 or Fe_2O_3/TiO_2, steep drop in phenol selectivity was observed using NiO. On the other hand, a NiO–Fe_2O_3 combined catalyst prepared by coprecipitation was also found to show high conversion while maintaining high phenol selectivity. This result implies that Ni–Fe complex oxide is closely related to the formation of active phase.

It is obvious that the calcination temperature is one of the most important factors which affects the catalytic activity and selectivity as shown in Table 3. Excellent catalytic performance was obtained at a calcination temperature of 800°C, exhibiting 93% in phenol selectivity with 100% in benzoic acid conversion. Rapid drop in conversion at a calcination temperature of 1000°C is obviously caused due to the decrease of surface area; however, the

TABLE 4

Effect of Ni/Fe Atomic Ratio on Conversion and Selectivity[a]

Catalyst[b]				Selectivity[c] (%)			
Ni/Fe[d] (atomic ratio)	NiO/NiFe$_2$O$_4$/Fe$_2$O$_3$[e] (molar ratio)	Surface area[f] (m^2/g)	Conversion (%)	Phenol	Benzene	CO + CO$_2$	Rate of phenol formation ($\times 10^{-5}$ mol/m$_2$ h)
0.25	0/1/0	6.2	62	25	75	tr.	1.13
0.50	0/1/0	5.8	79	10	68	17	0.61
0.75	0.5/1/0	7.8	67	78	13	5	3.02
1.00	1/1/0	6.1	100	88	12	tr.	6.49
1.63	2.3/1/0	3.8	94	86	11	2	9.57
2.00	3/1/0	2.7	46	73	15	8	5.60

[a] Reaction conditions: benzoic acid/air/steam/N$_2$ = 1/8/40/12 (molar ratio); space velocity = 1600 h^{-1}; reaction temperature = 400°C; catalyst weight = 20 g. The activities were measured after 3 h from the initial feed of benzoic acid.

[b] Prepared by precipitation; calcination temperature = 800°C.

[c] Calculated on the basis of moles benzoic acid converted.

[d] The values are based on the amounts of metal nitrates used for the catalysts preparation.

[e] The structures of oxides were identified by comparing their XRD spectra with those of NiO, NiFe$_2$O$_4$, and Fe$_2$O$_3$.

[f] The values are obtained by BET technique with nitrogen adsorption.

catalyst calcined at 700 and 600°C showed lower phenol formation rate normalized by surface area compared with that of catalyst calcined at 800°C. It is difficult to explain this result only from the effect of catalyst surface. The drastic influence of calcination temperature on activities of precipitated catalysts might be attributed to the differences of both physical and chemical structures. It is noteworthy that no phenol was formed and complete oxidation to CO and CO$_2$ was accelerated in the use of the catalyst calcined at 400°C.

Structural difference between the catalysts calcined at 800 and 400°C was revealed by characterization studies using XRD (Fig. 2). Low crystallinity of the catalyst calcined at 400°C is apparent from the broad peaks. In contrast, the catalyst calcined at 800°C shows very sharp peaks, indicating that the catalyst had a well-defined crystal structure. In comparison with the reference patterns, it is obvious that the catalyst calcined at 800°C consists of NiO and NiFe$_2$O$_4$. Fe$_2$O$_3$ itself did not exist in the

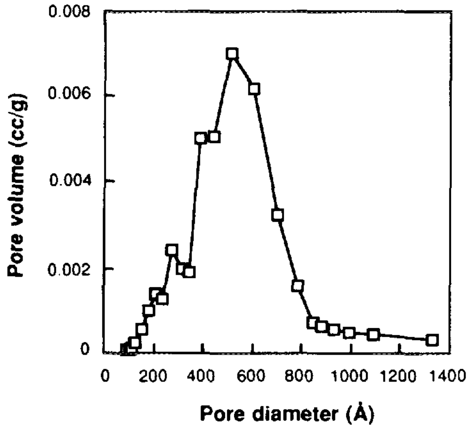


FIG. 3. Pore size distribution of the catalyst. Catalysts: NiO–NiFe$_4$O$_4$ (Ni/Fe atomic ratio = 1); prepared by precipitation; Calcination temperature = 800°C.

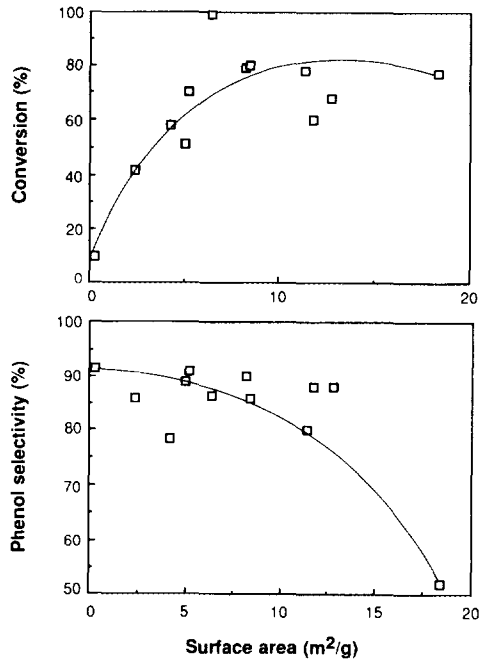
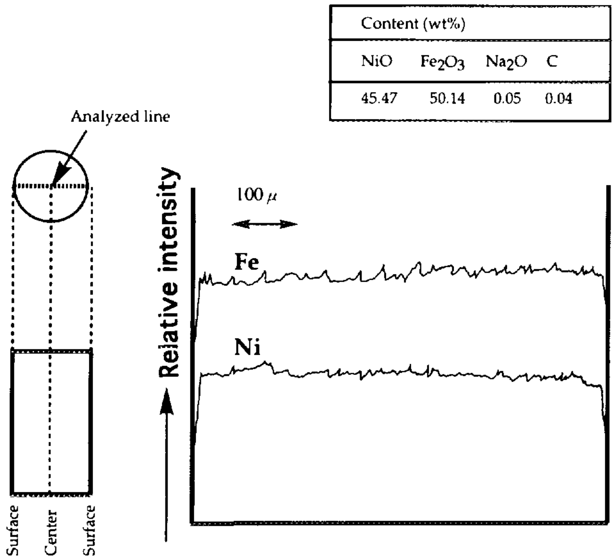


FIG. 4. Relations between surface areas and activity of the catalysts. Reaction conditions: Benzoic acid/air/steam/N$_2$ = 1/8/40/12; space velocity = 3200 h^{-1}; reaction temperature = 400°C. Catalysts: NiO–NiFe$_2$O$_4$ (Ni/Fe atomic ratio = 1); prepared by coprecipitation; calcined at 800°C.



Content (wt%)			
NiO	Fe_2O_3	Na_2O	C
45.47	50.14	0.05	0.04

FIG. 5. Distribution of Ni and Fe on catalyst (Ni/Fe = 1).

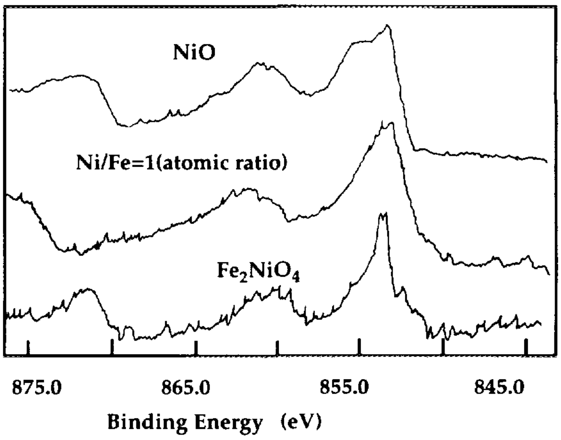


FIG. 7. XPS spectra of Ni2$p_{3/2}$ level of the catalyst and reference compounds.

catalysts at all. These results lead to an assumption that the inverse spinel structure of $NiFe_2O_4$ is the active species for phenol production. It has been reported that several kinds of complex oxides which have normal or inverse spinel structures show catalytic activities for hydrocarbon oxidation (28–32).

To confirm this assumption, it seems to be profitable to examine several catalysts which consist of different phases. From the results of XRD pattern, it might be considered that the formation of $NiFe_2O_4$ which has an inverse spinel structure is relevant to an active phase formation; however, the catalyst with the atomic ratio of Ni to Fe of 0.50 with $NiFe_2O_4$ single-phase results in a poor phenol formation rate as shown in Table 4. This result indicates that single-phase $NiFe_2O_4$ 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 formation rate. On the contrary, the catalysts that consist of NiO and $NiFe_2O_4$ gave relatively high phenol formation rate, indicating that two kinds of these oxides are necessary for the formation of active sites. Particularly, the catalyst with the atomic ratio of Ni to Fe of 1, namely equimolar quantities of NiO and $NiFe_2O_4$, exhibited an excellent 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 $NiFe_2O_4$. As shown in Fig. 3, the mean pore diameter of the catalyst with the atomic ratio of Ni to Fe of 1 is approximately 50 nm and the surface area is 6.1 m^2/g (Table 3). These results imply that the reaction proceeds on the surface of metal oxides or in the macropores of the catalysts. Figure 4 indicates that the surface area is surely one of the important factors for catalyst activity. Appropriate surface area is revealed to be 5–10 m^2/g to obtain both high conversion and high phenol selectivity. This result suggests that an increase in micropores or mesopores of the catalysts is not effective for the selective formation of phenol, implying that too strong adsorption of benzoic acid in the micropores or mesopores accelerates the complete oxidation to CO and CO_2.

EPMA analysis shown in Fig. 5 demonstrates a very homogeneous profile of the catalyst. In conjunction with the quantitative analysis, nickel and iron are distributed uniformly from the surface to the center of the catalyst. Since the composition of the catalyst surface is considered to be more important for catalyst activity than that of bulk, the relationship of the component between the surface and the bulk was analyzed by EPMA and XPS. The linear

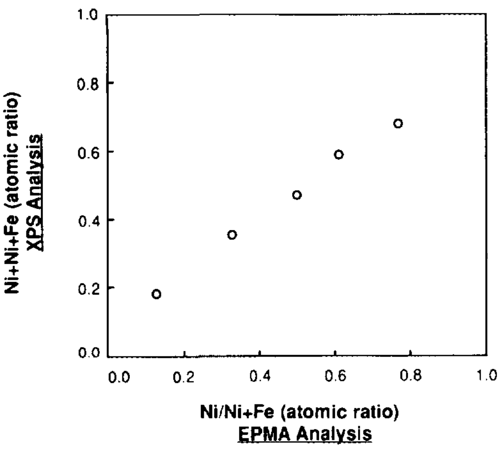


FIG. 6. Composition analyses of the surface and the bulk of the catalysts.

correlation in Fig. 6 indicates that the elemental composition of the bulk is proportional to that of the surface. Thus it is proved that the surface composition reflects the mass component in the catalyst preparation.

Furthermore, the medium shape and width of the XPS spectra of Ni2$p_{3/2}$ level shown by the catalyst (Ni/Fe = 1) suggests that two kinds of oxides, namely NiO and $NiFe_2O_4$, exist on the surface of the catalyst. As mentioned in Table 4, $NiFe_2O_4$ itself is not an active species for the formation of phenol. In addition, NiO-rich catalysts, e.g., those with a molar ratio of NiO to $NiFe_2O_4$ of 3, exhibit low conversion because of the low surface area. These results support an assumption that NiO dispersed finely in $NiFe_2O_4$ is an active species for phenol formation.

CONCLUSION

As a result of this work, we have discovered that NiO and Fe_2O_3 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 Fe_2O_3 is also found to exhibit high conversion maintaining high phenol selectivity. Especially, coprecipitation method is effective for the enhancement of catalyst activity. The catalyst with Ni/Fe atomic ratio of 1 and with the surface area from 5 to 10 m^2/g exhibit excellent activity for the vapor phase oxidation of benzoic acid to phenol. The homogeneous distribution profile of NiO and $NiFe_2O_4$ on the surface of the catalyst is found to be effective for the enhancement of catalytic activity.

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