Novel Catalyst Systems for Phenol Synthesis by Vapor Phase Oxidation of Benzoic Acid

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Nickel, iron, and cobalt oxides showed excellent catalytic activities for the vapor-phase oxidation of benzoic acid to phenol at the reaction temperature of 400 °C. The combination of these metal oxides, catalyst preparation by precipitation followed by calcination at 800 °C, and addition of Na_2O to the catalyst about 1% by weight enhanced the conversion of benzoic acid and the selectivity to phenol.

The structure of precipitation catalyst, Fe/Ni atomic ratio on the catalyst surface and formation of sodium benzoate on the catalyst surface play important roles for the optimization of catalyst activity. The novel catalyst systems could throw a new light on a one-step phenol synthesis from toluene. Appreciable one-pass phenol yield was obtained using a binary catalyst system consisting of V_2O_5–K_2SO_4–TiO_2 and NiO–Fe_2O_3–Na_2O, in which V_2O_5–K_2SO_4/TiO_2 worked as a catalyst for toluene oxidation to benzoic acid and NiO–Fe_2O_3–Na_2O functioned as a catalyst for benzoic acid to phenol.

Phenol is one of the most important starting materials for various chemicals such as phenol resin, polycarbonate, aniline, and some agricultural chemicals. Total production of phenol in the world amounts to more than 4 million metric tons per year. Most of this phenol is produced by the cumene process, which is shown in Fig. 1(a). In the process, equimolar quantities of phenol and acetone are coproduced from benzene and propylene via α-cumyl hydroperoxide. The overall phenol yield is estimated to be more than 90% and this is an effective process because of its mild reaction conditions. However, the process has a fundamental disadvantage that the price of phenol greatly depends on the acetone demand. Recently, a crucial problem has arisen: Methyl methacrylate production by oxidation of C_4-hydrocarbons[1)] is reducing the acetone demand drastically. From this point of view, the development of an alternative process for phenol synthesis as the only product has been strongly desired.

Among several processes (Fig. 1), direct oxidation of benzene to phenol (Fig. 1(e)) is the most attractive process. It is one of the ten challenges that typify the present needs of industrial catalysts.[2)] However, the phenol yield or space time yield still remains at a very low level, although a variety of methods have been proposed in order to form OH radicals or specific O^- species using H_2O_2, N_2O, or photocatalyst.[3)—14)] The direct hydroxylation of benzene is technically very difficult although it is very challenging. Commercial production by other processes shown in Fig. 1 is considered to be difficult from economical points of view, although benzene oxychlorination process (Fig. 1(d))

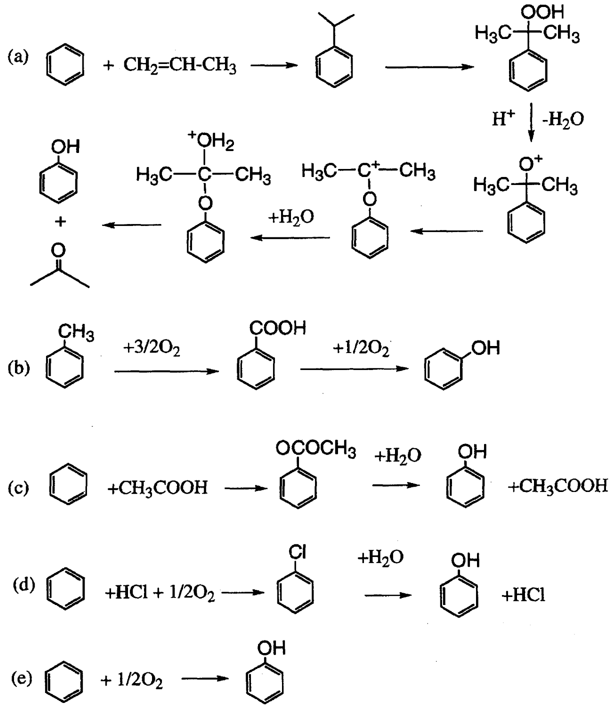

Fig. 1. Various routes for phenol production. (a) cumene process; (b) Dow process; (c) benzene acetoxylation process; (d) benzene oxychlorination process; (e) benzene direct oxidation process.

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was once industrialized for a short period. At present, the toluene oxidation to phenol via benzoic acid (Dow process, Fig. 1(b)) is the only alternative process which is in practical operation. At least three firms: New Nippon Phenol, DSM, and Kalama Chemical employed this process.[15)] The process is two-stage liquid-phase oxidation process, in which toluene is first oxidized to benzoic acid using Co–Mn catalyst, and then in the second stage, the benzoic acid is further oxidized to phenol using Cu catalyst.[16—21)] However, the process is reported to be subject to operational difficulties due to formation of tars, deactivation of Cu catalyst and low yield of phenol in the second reaction step. These are considered to be the main reasons for its inferiority to the cumene process. In spite of further development of modified Cu catalysts, the phenol yield still has much room for improvement. In order to solve these problems, the vapor-phase oxidation of benzoic acid has been widely investigated since Lummus developed CuO/ZrO catalyst.[22—30)] In general, a vapor phase process is more preferable than a liquid phase process from an industrial point of view, because the former is simpler with respect to catalyst regeneration and product purification. Although a variety of CuO-based catalysts have been proposed for the vapor phase oxidation of benzoic acid, high phenol yields have rarely been obtained. Presumably the deactivation is the most serious problem to be solved. According to one report,[24)] the sintering of CuO is responsible for the deactivation.

For the purpose of solving such problems, we have performed some research with a new concept about the improvement of catalyst. Looking at transition metal oxides, each of which might have catalytic activities for the vapor phase oxidation of benzoic acid to phenol,[31—35)] we discovered that not only CuO but also NiO, Co_3O_4, Fe_2O_3 have excellent catalytic activities for phenol formation from benzoic acid at a reaction temperature of 400 °C. We previously reported that nickel or iron oxides showed relatively high catalytic activities for the reaction.[31—35)] In this paper, we will show the results of further investigation for the new catalyst system and will describe in detail about the features of the new catalyst system including speculation about the reaction mechanism. Furthermore, efficiency of the new catalyst was demonstrated in terms of one-step phenol synthesis.

Experimental

The Preparation of Catalysts. Various kinds of nickel, iron, and cobalt oxide catalysts were prepared by ordinary impregnation or precipitation methods. The supported catalysts were prepared by impregnation of TiO_2 (anatase form, Merck, particle size 20—40 mesh) with aqueous solutions of metal nitrates, carbonates or ammonium metavanadate as follows. Ten mmol of metal salt was dissolved in 50 ml of ion-exchanged water, and a prescribed amount of TiO_2 was added thereto to give 5 or 10% of metal oxides' loading. After being dried at 100 °C for 24 h, the catalyst was then calcined at 500 °C for 3 h.

A precipitation method with aqueous solutions of metal nitrates and sodium hydroxide was also used. Water solution of nickel nitrate and/or iron nitrate (500 ml; 1 $mol\,dm^{-3}$) and water solution of sodium hydroxide (500 ml; 1 $mol\,dm^{-3}$) were added dropwise simultaneously into 1 dm^3 of cooled water while pH was maintained at 7.5. After stirring for 2 h at room temperature, the slurry was filtered. The precipitates obtained were washed with pure water until they became free from sodium, dried at 110 °C for 24 h and then calcined in air at 500—800 °C for 4 h. Additions of sodium to the nickel, iron, and cobalt catalysts were performed by impregnating with aqueous solutions of sodium carbonates and then the catalysts were calcined again in air at 500 °C for 3 h. Each catalyst was pulverized to the particle range of 20—40 mesh before use.

Apparatus and Procedure. The reaction was carried out using a conventional flow-type reactor at atmospheric pressure. The reactor was made of a quartz tube with an inner diameter of 20 mm and a length of 500 mm. Molten benzoic acid was supplied to the reactor with a hot steel syringe which was heated to 130 °C. Steam and toluene were fed with a plunge-type pump to the preheating zone, kept at 120 °C and were vaporized before injection to the catalyst zone. The same catalyst amount (10 g) was used for each reaction. The reaction temperature was measured by a thermocouple placed in a thermowell within the catalyst bed. The organic products were collected as follows: Initially the product gas was bubbled through acetone at about 0 °C and then trapped again by a Dry Ice–methanol cold trap system at about −70 °C. All the collected products were gathered and analyzed by a gas chromatograph using a flame ionization detector. Gaseous products were analyzed by a online gas chromatograph using a thermal conductivity detector. The selectivities of the products were calculated on the basis of benzoic acid converted. 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.

Results and Discussion

Catalytic Activities of Various Oxides Supported on TiO_2. Table 1 exhibits the catalytic performance of several kinds of oxides which were supported on TiO_2. At 300 °C, CuO showed fairly high phenol selectivity and benzoic acid conversion, while at 350 °C the rapid decrease in phenol selectivity and steep rise in benzene selectivity were observed. The most striking aspect was that NiO, Fe_2O_3, and Co_3O_4 exhibited appreciable activity for phenol formation at 400 °C. It is of great interest that NiO, Fe_2O_3, and Co_3O_4 exhibited activities of partial oxidation, because these oxides along with CuO have been regarded to be combustion catalysts.[36)] Although the conversion of benzoic acid by these oxides were recognized to be very low compared with that by CuO, phenol selectivity (See Table 1, footnote c)) was revealed to be fairly high, especially using NiO and Co_3O_4 catalysts. Among the novel catalyst systems, Fe_2O_3 catalyst exhibited relatively high conversion compared with that of NiO and Co_3O_4, while it showed lower phenol selectivity.

Table 1. Activities of Various Catalysts for Oxidation of Benzoic Acid[a)]

Catalyst	Temperature	Space velocity	Conversion	Selectivity (%)[c)]		
	°C	h^{-1}	%	Phenol	Benzene	CO+CO_2
5 wt% CuO/TiO_2[b)]	300	2060	66.3	68.8	22.5	5.5
	350	2060	81.7	16.8	64.4	16.2
10 wt% NiO/TiO_2	300	3200	Tr	Tr	Tr	Tr
	400	3200	6.3	72.3	12.4	10.5
10 wt% Fe_2O_3/TiO_2	300	3200	Tr	Tr	Tr	Tr
	400	3200	17.6	41.3	46.5	12.2
5 wt% Co_3O_4/TiO_2	300	3200	Tr	Tr	Tr	Tr
	400	3200	9.5	91.6	8.0	0.1
5 wt% V_2O_5/TiO_2	400	3200	1.0	0.0	23.0	75.0
5 wt% NiO-5 wt% Co_3O_4/TiO_2[b)]	400	2060	13.0	74.8	11.5	11.7
5 wt% Fe_2O_3-5 wt% Co_3O_4/TiO_2[b)]	400	2060	13.0	83.3	16.4	0.2
5 wt% NiO-5 wt% Fe_2O_3/TiO_2[b)]	400	2060	13.7	82.0	14.7	3.9

a) Reaction conditions: benzoic acid/air/steam/N_2=1/2/30/10 (molar ratio); benzoic acid 2.74×10^{-4} mol min^{-1}; catalyst weight=4.0 g. b) Benzoic acid/air/steam/N_2=1/2/15/10 (molar ratio). c) Selectivity is calculated on the basis of moles of benzoic acid converted.

The combination of Fe_2O_3 with NiO or Co_3O_4 gave a rise in conversion compared with conversion by NiO or Co_3O_4 monoxide catalyst with maintaining high phenol selectivity, while the combination of NiO and Co_3O_4 resulted in a little lower phenol selectivity due to a relatively large CO+CO_2 formation. V_2O_5 catalysts which are commonly used for partial oxidation of hydrocarbon showed no activity for phenol formation. Only 1% in conversion and a high selectivity for CO_2 (75%) was given as shown in Table 1.

The Effect of O_2 Partial Pressure on Catalytic Activities of Titania-Supported Catalysts. Figure 2 shows the effect of partial pressure of O_2 on catalytic activities of titania-supported NiO, Fe_2O_3, and Co_3O_4 catalysts. The rapid increase in the conversion of benzoic acid with increasing O_2/benzoic acid molar ratio was observed especially using Fe_2O_3 catalyst, while NiO catalyst exhibited only a slight change in benzoic acid conversion. Selectivities shown by Co_3O_4 and Fe_2O_3 were found to be very sensitive to O_2 partial pressure; the complete combustion reaction proceeded rapidly with increasing O_2/benzoic acid molar ratio, while NiO catalyst showed little change in selectivities with increasing O_2 partial pressure. On the other hand, according to the Lummus patent,[22)] O_2 molar ratio (O_2/benzoic acid) is strictly restricted below 1.5 in vapor-phase oxidation of benzoic acid using conventional CuO catalyst in order to maintain high phenol selectivity. These results suggest that an increase of O_2 partial pressure is subject to a rapid decrease of phenol selectivity with promoting deeper oxidation of phenol to CO_2. It means that care should be paid to O_2 partial pressure in order to maintain high phenol selectivities. Therefore, the little dependence of phenol selectivity on O_2 partial pressure shown by NiO is considered to be a very desirable feature from practical and operational points of view.

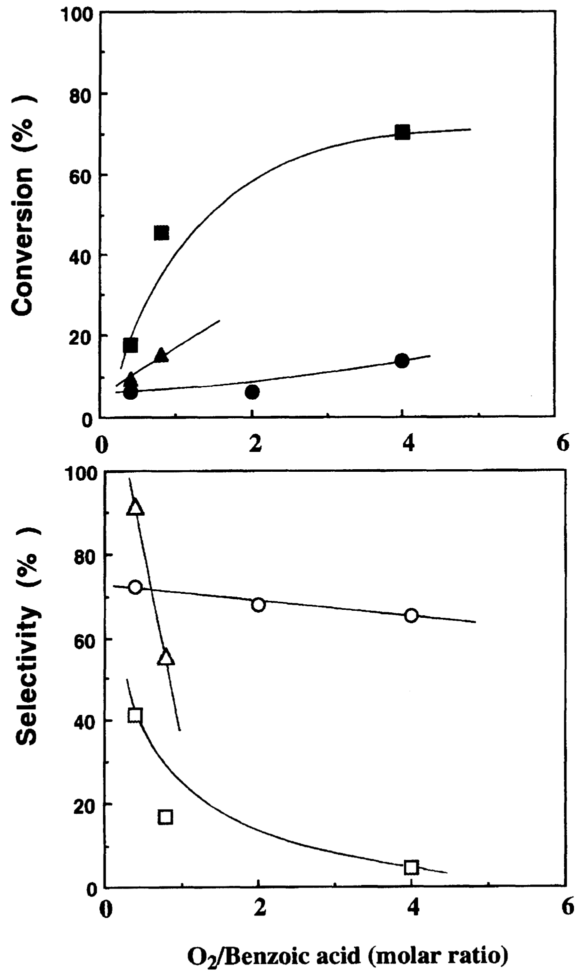


Fig. 2. Effect of O_2/Benzoic acid molar ratio on catalytic activities. Reaction conditions: Benzoic acid/air/steam/N_2 = 1/x/30/10 (molar ratio); benzoic acid 2.74×10^{-4} mol min^{-1}; catalyst weight = 4.0 g; calcination temperature = 500 °C; reaction temperature=400 °C; ●○: 10 wt% NiO/TiO_2; ▲△: 5 wt% Co_3O_4/TiO_2; ■□: 10 wt% Fe_2O_3/TiO_2.

Activities of Precipitation Catalysts. Catalysts prepared by a precipitation method were also used for the reaction. Table 2 shows the results of their activity tests. Fe_2O_3 catalyst exhibited the highest conversion among Fe_2O_3, NiO, and Co_3O_4, as is the same in the impregnation catalysts shown in Table 1. Almost the same value and the same order ($Fe_2O_3 < NiO < Co_3O_4$) of phenol selectivity were obtained as in the impregnation catalysts shown in Table 1. These results indicate that the effect of titania-support is not so large in the reaction.

The complex oxides prepared by coprecipitation exhibited a higher activity than single oxides did. The efficiency of the combination was the same catalytic feature as was shown by the impregnated catalysts in Table 1. The combination of NiO and Fe_2O_3 enhanced benzoic acid conversion drastically while maintaining relatively high phenol selectivity; but the combination of Co_3O_4 and Fe_2O_3 resulted in a decrease in phenol selectivity with almost the same conversion as that of the impregnated catalyst. The reason for the excellent effect of Ni–Fe combination has not been clarified yet, but several aspects of Ni–Fe catalysts prepared by precipitation have been reported in our previous paper:[33,35] 1) The catalyst with the atomic ratio of nickel to iron of 1 showed an optimum phenol selectivity and an optimum benzoic acid conversion. 2) Calcination temperature of the precipitation catalyst was found to be one of the most important factors which affect catalytic activities. A maximum phenol selectivity and a maximum benzoic acid conversion were obtained around the calcination temperature of 800 °C. 3) The precipitation catalysts calcined at 800 °C consist of two kinds of oxides, namely NiO and $NiFe_2O_4$. These results could lead to an assumption that NiO dispersed on $NiFe_2O_4$ is an active species.

Moreover, addition of alkali metal oxides to the complex oxide catalysts was highly effective in enhancing both benzoic acid conversion and phenol selectivity as is also reported in our previous paper.[34] When we examined Na_2O, K_2O, CaO, and MgO as additives in that paper, Na_2O was found to be the most effective for the enhancement of catalyst performance. In particular, Na_2O-promoted NiO–Fe_2O_3 catalyst showed 91% phenol selectivity with 100% conversion as shown in Table 2. Enhancement of conversion and phenol selectivity by sodium addition is believed to be due to acceleration of the adsorption of benzoic acid on the catalyst to form sodium benzoate which is presumed to be an intermediate to phenol.[34] Consequently, the most efficient catalyst, thus far, is Na_2O-promoted NiO–Fe_2O_3 catalyst.

Here, the relations between structure of catalyst and catalyst activity were investigated in more detail using NiO–Fe_2O_3–Na_2O catalysts. Table 3 elucidates the relations between calcination temperature and physical structure or catalytic activities of NiO–Fe_2O_3–Na_2O catalyst. The decrease in benzoic acid conversion was observed with the increase in calcination temperature or calcination time. This was probably due to the decrease in specific surface area. In contrast, phenol selectivity increased linearly with an increase in calcination temperature.

It is noteworthy that the drastic changes both in catalytic activity and in physical structure of the catalyst were observed at the temperature between 600 and 700 °C. Average pore diameters were doubled, with surface area diminishing to half. Marked enhancement in phenol selectivity was given concurrently by the 100 degrees' rise of calcination temperature from 600 °C. The XRD patterns shown in Fig. 3 revealed that formation of $NiFe_2O_4$ which has the inverse spinel structure proceeded rapidly above the calcination temperature of 600 °C. At the calcination temperature of 700 °C, the catalyst was proved to consist of only two kinds of oxides,

Table 2. Activities of Catalysts Prepared by Precipitation for Oxidation of Benzoic Acid[a)]

Catalyst	Calcination temperature	Reaction temperature	Space velocity	Conversion	Selectivity (%)[e)]		
	°C	°C	h^{-1}	%	Phenol	Benzene	$CO+CO_2$
Fe_2O_3	500	370	8800	33.7	52.2	45.2	2.1
NiO[b)]	600	400	3500	17.0	63.8	8.7	25.6
Co_3O_4[b)]	500	400	8200	10.0	85.5	5.8	6.8
50 wt% Fe_2O_3–50 wt% NiO	500	370	5280	49.6	63.0	28.5	7.5
50 wt% Fe_2O_3–50 wt% NiO[c)]	800	400	10000	42.6	66.0	15.8	17.9
82 wt% Fe_2O_3–18 wt% Co_3O_4	500	370	8000	14.8	32.0	47.2	16.9
50 wt% Fe_2O_3–50 wt% Co_3O_4[c)]	800	400	8000	14.9	30.5	50.3	18.2
51.5 wt% Fe_2O_3–47.5 wt% NiO–1 wt% Na_2O[c)]	800	400	10000	100	91.1	7.8	1.9
51.5 wt% Fe_2O_3–47.5 wt% NiO–1 wt% Na_2O[d)]	800	400	2857	80.4	47.1	22.4	9.0

a) Reaction conditions: Benzoic acid/air/steam/N_2=1/2/30/10 (molar ratio); benzoic acid 2.74×10^{-4} mol min^{-1}; catalyst weight=4.0 g. b) Benzoic acid/air/steam=1/4/20 (molar ratio); benzoic acid 2.74×10^{-4} mol min^{-1}; catalyst weight=10.0 g. c) Benzoic acid/air/steam=1/5/15 (molar ratio); Benzoic acid 1.02×10^{-3} mol min^{-1}; catalyst weight=10.0 g. d) Benzoic acid/air/steam=1/5/0 (molar ratio); Benzoic acid 1.02×10^{-3} mol min^{-1}; catalyst weight=10.0 g; selectivity of phenyl benzoate=18.5%; selectivity of biphenyl=3.0%. e) Selectivity is calculated on the basis of moles of benzoic acid converted.

Table 3. Relation between Calcination Temperature and Structure or Catalytic Activities[a)]

Calcination temperature	Calcination time	Surface area[b)]	Average pore diameter[b)]	Conversion	Selectivity(%)[c)]		
°C	h	$m^2\ g^{-1}$	nm	%	Phenol	Benzene	$CO+CO_2$
500	3	38.9	14.0	100	32.4	60.7	6.0
500	13	34.5	15.0	100	37.0	56.8	5.8
600	3	27.5	16.1	93.1	42.2	53.3	4.2
700	3	16.5	32.6	84.2	68.4	26.9	4.1
700	13	15.3	33.6	85.1	70.7	23.1	5.8

a) Reaction conditions: catalyst 49.5 wt% NiO–49.5 wt% Fe_2O_3–1 wt% Na_2O; catalyst weight = 10.0 g; benzoic acid/air/steam = 1/5/25 (molar ratio); SV = 3500 h^{-1}; reaction temperature = 410°C. b) The value were caluculated by BET technique with nitrogen adsorption. c) Selectivity is calculated on the basis of moles of benzoic acid converted.

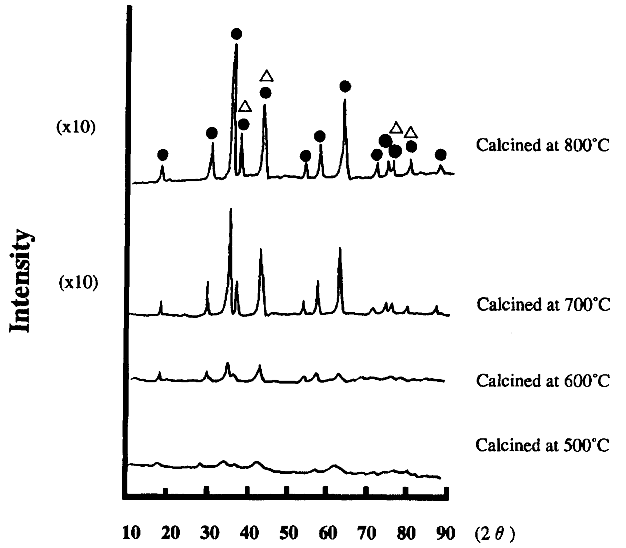


Fig. 3. XRD patterns of the catalysts of different calcination temperature: (△) NiO, (●) $NiFe_2O_4$.

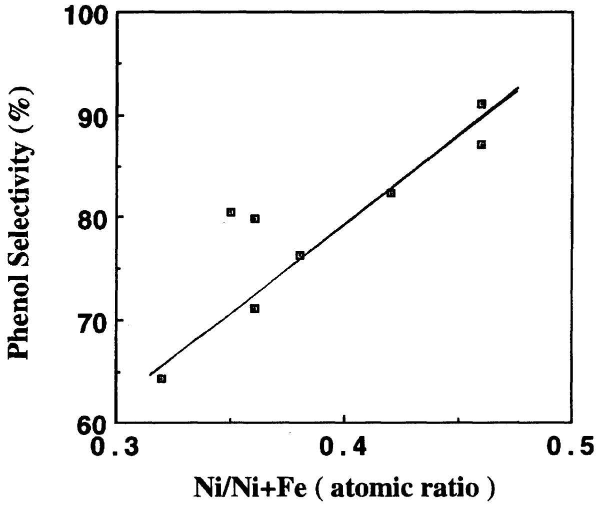


Fig. 4. Relation between phenol selectivities and Ni concentration on the catalyst surface. Catalyst: 49.5 wt% NiO–49.5 wt% Fe_2O_3–1.0 wt% Na_2O. Reaction conditions: reaction temperature = 400 °C; calcination temperature = 800 °C; benzoic acid/air/steam = 1/4/20 (molar ratio); SV = 3500 h^{-1}. Ni/Ni+Fe atomic ratio was measured by XPS analysis.

namely NiO and $NiFe_2O_4$. These results support the assumption that dispersed NiO on $NiFe_2O_4$ are active species, and that the structure of the catalyst plays an important role for the optimization of catalyst activities.

Much importance should be attached to the reproducibility of catalyst activity, because it is generally considered that the reproducibility of the precipitation catalyst is difficult to obtain for some reactions. Actually, several different catalysts' activities were obtained for this reaction, especially in phenol selectivities, in spite of compositions of the catalysts being the same. XPS analysis revealed that differences of Ni/Ni+Fe molar ratio on catalysts' surface were brought about depending on the catalysts, in spite of the compositions being the same as in the bulk. Figure 4 depicts the relation between phenol selectivities exhibited by 49.5 wt% NiO–49.5 wt% Fe_2O_3–1 wt% Na_2O and Ni/Fe atomic ratio on a catalyst surface. Apparently, the phenol selectivity increased with increasing NiO concentration. Since there seemed to be little difference in surface areas between these catalysts, the results indicate that the Ni/Fe atomic ratio affects catalytic activity strongly. As described above, the catalysts consist of two kinds of oxides: i. e. NiO and $NiFe_2O_4$; hence the difference of Ni/Fe atomic ratio on the catalyst surface indicates the difference of NiO or $NiFe_2O_4$ concentration. A relatively high concentration of NiO over $NiFe_2O_4$ is desirable to form phenol selectively.

Reaction Mechanism. The reaction mechanism over CuO catalyst was demonstrated in some papers.[27—30)] It is plausible that the reaction over the Na-promoted NiO–Fe_2O_3 catalyst proceeds basically on the same mechanism as that over the conventional CuO catalyst, as shown in Fig. 5. Initially, benzoic acid is adsorbed on the base component, Na_2O, on the surface of the catalyst, and is converted to sodium benzoate. It is then transformed into *o*-benzoylsalicylic acid which is the intermediate for phenol formation.[27—30)] At present, it is not clear that nickel benzoate shown in Fig. 5 is an intermediate to form *o*-benzoylsalicylic acid, but NiO

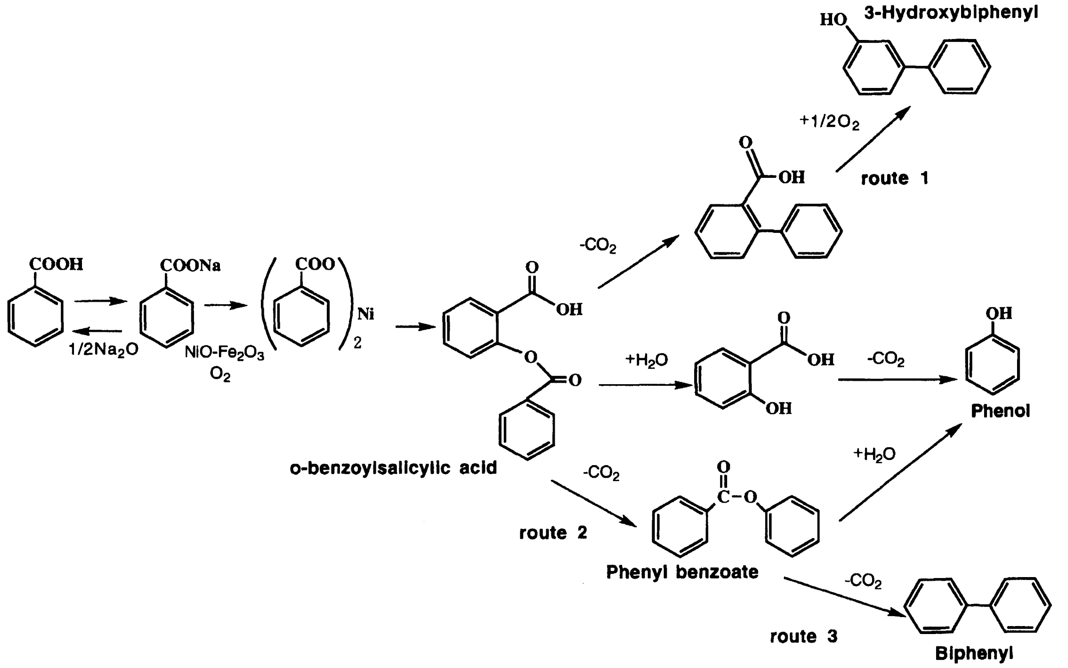


Fig. 5. The mechanism of phenol production over NiO–Fe_2O_3–Na_2O catalyst.

is presumed to be the main active sites for benzoic acid oxidation since appreciable dependence of phenol selectivity on Ni concentration on the catalyst surface was observed, as described in Fig. 4.

Two supplemental experiments were performed in order to confirm the reaction mechanism over the most excellent catalyst in terms of toluene conversion and phenol selectivity among the novel catalyst systems.

First, toluic acids were employed as starting materials; the results are given in Table 4. *m*-Cresol from *o*-toluic acid and *p*- or *o*-cresol from *m*-toluic acid were obtained over the NiO–Fe_2O_3–Na_2O catalyst although the cresol selectivity is rather low. These results indicate that hydrogen in the *o*-position of carboxyl group is substituted by an OH group. This supports the mechanism of the oxidation of benzoic acid to phenol over NiO–Fe_2O_3–Na_2O shown in Fig. 5.

Secondly, by-products formed in the reaction were identified using a GC-MS instrument. The characteristic distribution of the by-products could be a clue for the reaction mechanism. In addition, the detailed identification of by-product in the reaction is very important information in terms of phenol purification, because phenol is mainly used as a raw material of resins. Impurities content greatly affects the polymerization reaction or the characteristics of the resins. Organic products collected in cold traps were vacuum-distilled and divided into fractions to remove main identified components such as benzoic acid, phenol and benzene. Each fraction including residue was analyzed and trace amounts of components such as phenyl benzoate, biphenyl, and 3-hydroxybiphenyl were identified. The detection of phenyl benzoate supports the pathway of route 2. Furthermore, the observed rapid increase in phenyl benzoate formation in the absence of steam[37] shown in Table 2 ensures the existence of this route. It is reported that biphenyl or diphenyl ether was obtained in several % of selectivities using CuO catalysts,[27,28] while no diphenyl ether and trace amounts of biphenyl were formed over the NiO, Fe_2O_3, or Co_3O_4 catalysts. This characteristic results imply that in the CuO catalyst system, further decarboxylation tends to proceed

Table 4. Vapor Phase Oxidation of Toluic Acid to Cresol[a]

Substrate	Conversion	Selectivity[b]/%				
	%	*o*-Cresol	*m*-Cresol	*p*-Cresol	Phenol	CO+CO_2
o-Toluic acid	73.4	Tr	9.1	0	23.1	2.1
m-Toluic acid	23.1	9.4	Tr	0.9	19.3	3.4

a) Catalysts: 47.5 wt% NiO–51.5 wt% Fe_2O_3–1 wt% Na_2O; prepared by coprecipitation; calcined at 800 °C. Reaction conditions: Toluic acid/toluene/air/N_2/steam=1/26/5/10/51 (molar ratio); space velocity = 3000 h^{-1}. b) Selectivity is calculated on the basis of moles of toluic acid converted.

along route 3 in Fig. 5, while, in the novel catalyst, very few reactions are supposed to proceed along route 3. Formation of 3-hydroxybiphenyl over novel catalyst implies the pathway of route 1, namely biphenyl-2-carboxylic acid was oxidized to 3-hydroxybiphenyl.

In vapor-phase oxidation, it is commonly recognized that consecutive oxidation of the products is the barrier for the enhancement of product selectivity. In order to compare the activity for consecutive oxidation exhibited by $NiO–Fe_2O_3–Na_2O$ catalyst with that exhibited by conventional CuO catalyst, phenol or benzaldehyde was used as a starting material in the reaction system. Table 5 indicates that the consecutive oxidation of phenol to CO or CO_2 proceeds only slightly over $NiO–Fe_2O_3–Na_2O$ catalyst, while CuO catalyst easily accelerates the oxidation of phenol to CO or CO_2. These results demonstrate the outstanding characteristic of $NiO–Fe_2O_3–Na_2O$ catalyst which exhibits the high phenol selectivity. In addition, it was confirmed that the high activity for consecutive oxidation of phenol is one of the serious problems in the conventional CuO catalyst which prevent enhancing the catalyst performance. It is also noteworthy that benzaldehyde, which could be easily oxidized to benzoic acid, is converted to phenol in fairly high selectivity in the vapor-phase oxidation using $NiO–Fe_2O_3–Na_2O$ catalyst (Table 5). Large amount of benzaldehyde formation as a by-product is expected in the vapor-phase oxidation of toluene to benzoic acid using V_2O_5 catalyst. Therefore, if we consider one-pass toluene conversion to phenol using binary catalyst system, such activity of $NiO–Fe_2O_3–Na_2O$ catalyst for benzaldehyde is a very desirable feature.

One-Pass Toluene Conversion to Phenol by Vapor Phase Oxidation. Although the yield of vapor-phase oxidation of toluene to benzoic acid still remains at a low level at present[38,39] compared with the liquid-phase oxidation,[40] one-pass conversion of toluene to phenol would be a very attractive process from an industrial point of view because vapor-phase reactions generally require lower fixed capital investment than that of liquid phase process. Several characteristic features shown by novel catalysts, such as the insensitivity of phenol selectivity against O_2 partial pressure, the inhibition to consecutive oxidation of phenol, very high phenol selectivity and high activity not only for benzoic acid but also for benzaldehyde, indicate the possibility of one-pass toluene conversion to phenol by the combination with V_2O_5 catalyst, which catalyzes the vapor-phase oxidation of toluene to benzoic acid.

In order to examine and confirm the possibility for one-pass toluene conversion to phenol, $V_2O_5–K_2SO_4–TiO_2$ and $NiO–Fe_2O_3–Na_2O$ catalysts were employed for the activity measurement. $V_2O_5–K_2SO_4–TiO_2$ catalyst has been commonly used for the vapor phase oxidation of naphthalene to phthalic

Table 5. Vapor-Phase Oxidation of Phenol or Benzaldehyde

Substrate	Catalyst	Conversion	Selectivity (%)[d]		
		%	Phenol	Benzene	$CO+CO_2$
Phenol	49.8 wt% NiO–49.8 wt% Fe_2O_3–0.4 wt% Na_2O[a]	3.7	—	6.5	93.2
	5 wt% CuO/TiO_2[b]	32.3	—	39.3	57.5
Benzaldehyde	50 wt% NiO–50 wt% Fe_2O_3[c]	75.3	62.1	19.6	7.3

a) Calcined at 800 °C. Reaction Conditions: benzoic acid/air/steam = 1/3.5/22 (molar ratio); reaction temperature = 400 °C; SV = 3900 h^{-1}; catalyst weight = 10.0 g. b) Prepared by impregnation; calcined at 500 °C. Reaction Conditions: Benzoic acid/air/steam = 1/5/15 (molar ratio); catalyst weight = 4.0 g; reaction temperature = 400 °C; SV = 3500 h^{-1}. c) Calcined at 800 °C. Reaction Conditions: Benzoic acid/air/steam/N_2=1/10/30/10 (molar ratio); reaction temperature=400 °C; SV=1070 h^{-1}; catalyst weight=20.0 g. d) Selectivity is calculated on the basis of molar phenol or benzaldehyde converted.

Table 6. One-Step Oxidation of Toluene to Phenol over Binary Catalyst System[a]

Toluene/Air/N_2/H_2O (molar ratio)	Reaction temperature	Conversion	Selectivity (%)[c]				
	°C	%	Benzoic acid	Benzaldehyde	Phenol	Benzene	$CO+CO_2$
1/10/1/31[b]	350	33.9	73.1	14.9	2.8	0.4	8.6
1/10/1/30[b]	400	25.0	44.1	—	11.9	21.3	19.0
1/5.2/1/30[c]	400	18.3	20.9	4.5	34.3	19.4	18.5
1/2.2/1/31[c]	400	15.4	—	3.0	63.9	15.7	9.1
1/5.0/15/30[d]	300	15.9	6.5	1.5	7.6	35.1	44.3

a) Catalyst: 5 g of 5 wt% V_2O_5–1 wt% K_2SO_4–TiO_2 for upper layer and 15 g of 49.8 wt% NiO–49.8 wt% Fe_2O_3–0.4 wt% Na_2O. b) Toluene feed=2.14 mmol g-cat^{-1} h^{-1}. c) Toluene feed=2.93 mmol g-cat^{-1} h^{-1}. d) Catalyst; 5 g of 5 wt% V_2O_5–1 wt% K_2SO_4–TiO_2 for upper layer and 5 g of 5.0 wt% CuO–TiO_2; toluene feed=3.15 mmol g-cat^{-1} h^{-1}.

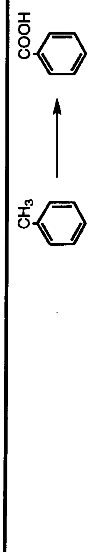
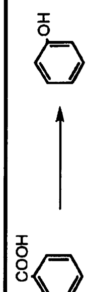
anhydride.[41] Table 6 shows the results of vapor phase oxidation of toluene to phenol using 5 g of V_2O_5–K_2SO_4–TiO_2 for upper layer and 15 g of NiO–Fe_2O_3–Na_2O catalyst for lower layer. At the temperature of 350 °C, benzoic acid was formed in 73.1% selectivity, while trace amounts of phenol was produced because NiO–Fe_2O_3–Na_2O catalyst did not function. At the temperature of 400 °C, 11.9% of phenol selectivity was obtained due to the two kinds of catalyst which functioned. With decreasing O_2/toluene (air/toluene) molar ratio, the phenol selectivity rose while the toluene conversion fell. At the air/toluene molar ratio of 2.2, 63.9% of phenol selectivity was obtained. On the other hand, CuO–V_2O_5 catalyst system, only poor phenol selectivity was obtained. The reason is supposed to be the further consecutive oxidation of benzoic acid over CuO catalyst. These phenomena were in agreement with the results of the catalytic feature of consecutive oxidation shown in Table 5.

Table 7 shows the comparison of the results for phenol synthesis from toluene obtained by liquid-phase process (Dow process) with the results obtained by vapor-phase process proposed in this paper. Total selectivity of phenol from toluene in the proposed process is lower than that of conventional liquid-phase process; however, there are several advantages for the proposed process such as low facility investment and simplicity of catalyst separation. Therefore, further calculation is needed in order to evaluate the efficiency of the process correctly. But it could be possible that the development of more efficient V_2O_5-based catalysts for vapor-phase oxidation of toluene to benzoic acid would lead to the establishment of a vapor-phase process for phenol synthesis which is free from dependency on by-product acetone.

Conclusion

It was found that Fe_2O_3, Co_3O_4, and NiO showed excellent catalytic activity for the vapor phase oxidation of benzoic acid to phenol. In addition, the combination of these oxides improved catalytic activity with maintaining a high phenol selectivity. Precipitation and the addition of sodium component were found to be very effective for the enhancement of conversion. Calcination temperature was revealed to be one of the important factors for the optimization of catalytic activity, which was believed to be caused by both appropriate physical structure and concentration of active species. The excellent performance of the novel catalyst was proved to be applicable to one-step phenol production in vapor-phase oxidation with the combination of NiO–Fe_2O_3–Na_2O catalyst and V_2O_5-based catalyst. The one-step conversion of toluene to phenol is expected to contribute greatly for the establishment of a simpler process for phenol synthesis.

Table 7. Comparison of Process for Phenol Synthesis

							
Process	Catalyst	Reaction temperature °C	Benzoic acid selectivity on the basis of toluene converted (%)	Catalyst	Reaction temperature °C	Phenol selectivity on the basis of benzoic acid converted (%)	Phenol selectivity on the basis of toluene converted (%)
Conventional Dow process (liquid phase)	Co, Mn	200	91.1[a)]	CuO	310	84.8[b)]	77.2
Proposed process (vapor phase)	V_2O_5–K_2SO_4	400		NiO–$NiFe_2O_4$–Na_2O	400		63.9[c)]

a) Taken from Ref. 40. b) Taken from Ref. 18. c) Taken from Table 6.

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