Vapour Phase Oxidation of Benzoic Acid to Phenol over NiO–Fe$_2$O$_3$ Catalysts

Jun Miki, Minoru Asanuma, Yakudo Tachibana, and Tsutomu Shikada*

Materials and Processing Research Center, NKK Corporation, Kawasaki-ku, Kawasaki 210, Japan

The NiO–Fe$_2$O$_3$ complex oxide catalysts, which were prepared by precipitation and then calcined at around 800 °C, showed excellent catalytic activity in the vapour phase oxidation of benzoic acid to selectively form phenol.

The oxidation of toluene to phenol *via* benzoic acid is used in the Dow process which is one of the conventional methods for the commercial production of phenol.[1] 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 a copper catalyst. However, with this copper catalyst there are a number of problems such as tar formation and catalyst deactivation,[2] both of which need to be improved. It has been reported that the vapour phase oxidation of benzoic acid to phenol proceeds on supported copper catalysts.[3] In the vapour system, although the formation of tar was reduced, the catalytic activity decreased after several hours reaction. Here we propose novel catalysts of NiO–Fe$_2$O$_3$ for the vapour phase oxidation of benzoic acid to phenol.

The titania-supported catalysts were prepared by impregnating a commercially available titania (Merck, particle size 20–40 mesh) with aqueous solutions of metal nitrates, followed by drying and then calcining in air at 500 °C for 3 h. NiO, Fe$_2$O$_3$ and NiO–Fe$_2$O$_3$ combined catalysts were prepared by precipitation with aqueous solutions of metal nitrates and sodium hydroxide. The precipitates obtained were washed with pure water until they became free from sodium, dried and then calcined in air temperatures of 400–800 °C for 4 h.

Using the NiO–Fe$_2$O$_3$ catalysts a small amount of phenol was produced from benzoic acid without packing the catalyst in the stainless steel reactor. This suggested that a stainless steel reactor surface would exhibit catalytic activity for phenol production. The titania-supported metal oxide catalysts such as NiO, Fe$_2$O$_3$, Cr$_2$O$_3$ and MoO$_3$ were also examined. NiO–TiO$_2$ and Fe$_2$O$_3$–TiO$_2$ exhibited considerable catalytic activity for phenol production while Cr$_2$O$_3$–TiO$_2$ and MoO$_3$–TiO$_2$ showed little activity (Table 1). The Fe$_2$O$_3$–TiO$_2$ catalyst gives higher conversion and lower phenol selectivity than the NiO–TiO$_2$ catalyst. The combination of NiO and Fe$_2$O$_3$ resulted in enhanced phenol selectivity. While the conventional CuO catalyst gave higher conversion levels compared to NiO or Fe$_2$O$_3$ at 400 °C, the phenol selectivity with the CuO catalyst was lower than that on NiO or Fe$_2$O$_3$ because of a large amount of benzene formation. This suggests that the oxidation potential of NiO or Fe$_2$O$_3$ is milder than that of CuO.

As shown in Table 1, the catalyst prepared by precipitation gave higher conversions than the titania-supported catalysts. In particular, NiO–Fe$_2$O$_3$ catalyst gave higher conversion levels while maintaining high phenol selectivity. These results indicate that the combination of NiO and Fe$_2$O$_3$ is essential for optimising conversion and selectivity. Table 2 shows the effect of calcination temperature on the NiO–Fe$_2$O$_3$ catalyst activity. It was found that the calcination temperature is one of the most important factors which affect catalytic activity and selectivity. An optimum phenol selectivity was obtained when the calcination temperature was 800 °C. The benzene selectivity, increased below 600 °C and above 1000 °C.

In order to clarify the structural differences between the catalysts calcined at 800 and 400 °C, the catalyst structures were examined by XRD. Low crystallinity of the catalyst calcined at 400 °C was apparent from the broad diffraction peaks. In contrast, the catalyst calcined at 800 °C showed very sharp peaks, indicating grown crystal structure. In comparison with reference patterns, it was found that the catalyst calcined at 800 °C consists of two kinds of oxides, NiO and NiFe$_2$O$_4$. These results lead to an assumption that the inverse spinel structure of NiFe$_2$O$_4$ 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 activity for hydrocarbon oxidation.[4]

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Table 2 Effect of calcination temperature on catalytic activity[a]

Calcination temperature (°C)	Conversion (%)	Selectivity (%)[b] Phenol	Benzene	CO + CO$_2$
400	—[c]	—[c]	—[c]	—[c]
600	94	51	44	3
700	76	53	14	30
800	100	93	5	1
1000	0.2	43	50	6

[a] Catalysts: 48 wt% NiO–52 wt% Fe$_2$O$_3$; prepared by coprecipitation. *Reaction conditions*: Benzoic acid/air/steam/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] Selectivity is calculated on the basis of moles benzoic acid converted. [c] Too much exothermic reaction proceeded to maintain a steady temperature.

Table 1 Activities of various catalysts for oxidation of benzoic acid[a]

Catalyst[b]	T/°C	Space velocity/ h^{-1}	Conversions (%)	Selectivity (%)[e] Phenol	Benzene	CO + CO$_2$
10 wt% NiO–TiO$_2$[c]	400	3200	6.3	72.3	12.4	10.5
10 wt% Fe$_2$O$_3$–TiO$_2$[c]	400	3200	17.6	41.3	46.5	12.2
5 wt% MoO$_3$–TiO$_2$[c]	400	3200	1.9	2.0	33.4	64.0
10 wt% Cr$_2$O$_3$–TiO$_2$[c]	400	3200	trace	trace	trace	trace
5 wt% CuO–TiO$_2$[c]	350	2060	81.7	16.8	64.4	16.2
5% wt% NiO–5 wt% Fe$_2$O$_3$–TiO$_2$[c]	400	2060	13.7	82.0	14.7	3.9
Fe$_2$O$_3$[d]	370	8800	33.7	52.2	45.2	2.1
NiO[d]	350	10570	20.5	16.7	8.5	74.5
50 wt% Fe$_2$O$_3$–50 wt% NiO[d]	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] Prepared by impregnation. [d] Prepared by precipitation. [e] Selectivity is calculated on the basis of moles benzoic acid converted.

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