

# Alkali-promoted NiO-Fe<sub>2</sub>O<sub>3</sub> Catalysts for Vapour-phase Oxidation of Benzoic Acid to Phenol

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Addition of Na<sub>2</sub>O to the NiO-Fe<sub>2</sub>O<sub>3</sub> catalyst system was found to be very effective for increasing the space-time yield of phenol while maintaining high phenol selectivity; a reaction route to phenol formation *via* sodium benzoate is proposed.

While copper is commonly used as a catalyst for the oxidation of benzoic acid to phenol in the Dow process, it suffers problems such as deactivation, tar formation and low STY (space-time yield).<sup>1</sup> In order to solve these problems we have already developed a novel catalyst system which consists of NiO and Fe<sub>2</sub>O<sub>3</sub>, and have achieved high benzoic acid conversion while maintaining high phenol selectivity.<sup>2</sup> Here we report modified NiO-Fe<sub>2</sub>O<sub>3</sub> with incorporation of alkali- or alkaline earth-metal oxides for the enhancement of STY.

NiO-Fe<sub>2</sub>O<sub>3</sub> catalysts were prepared by precipitation from aqueous solutions of metal nitrates upon addition of sodium hydroxide. The precipitates obtained were washed with pure water until they were free of sodium, they were then dried and calcined in air at 800 °C for 3 h. The catalysts were crushed to give particles of 20–40 mesh size range. Alkali- or alkaline earth-metal oxides were incorporated into the catalysts by addition of these to aqueous solutions of metal nitrates or carbonates. The reactions were carried out at atmospheric pressure using a continuous flow type reaction apparatus with a fixed catalyst bed. The reactor was made of a quartz tube with an inner diameter of 20 mm and a length of 500 mm.

As shown in Table 1, the NiO-Fe<sub>2</sub>O<sub>3</sub> catalyst showed 93% phenol selectivity with 100% conversion at a space velocity (SV) of 1600 h<sup>-1</sup>. Increasing the SV to 10 000 h<sup>-1</sup>, led to a drastic decrease in conversion and the phenol selectivity also decreased as a result of benzene formation. Addition of Na<sub>2</sub>O, K<sub>2</sub>O, CaO or MgO to the NiO-Fe<sub>2</sub>O<sub>3</sub> catalyst was examined under an SV of 10 000 h<sup>-1</sup>. It was found that addition of Na<sub>2</sub>O was most effective in enhancing both benzoic acid conversion and phenol selectivity. The Na<sub>2</sub>O-promoted catalyst gave high [1300 g (l cat)<sup>-1</sup> h<sup>-1</sup>] STY, *i.e.* more than three times that of the catalyst in the absence of additive. Although the addition of K<sub>2</sub>O, CaO or MgO also enhanced phenol selectivity, the STY was only marginally improved. It is noteworthy that extremely high phenol selectivity is achieved by the addition of CaO.

We propose a mechanism for catalysis of the reaction over NiO-Fe<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O as shown in Fig. 1.<sup>3</sup> Initially, benzoic acid is adsorbed on the base component, Na<sub>2</sub>O, on the surface of the catalyst and is converted to sodium benzoate. It is then transformed into benzoyl salicylic acid which is the intermediate for phenol formation. Enhancement of conversion by the additives is believed to be due to acceleration of the

adsorption of benzoic acid on the catalyst to form alkali- or alkaline earth-metal benzoates while the increase of phenol selectivity is presumed to be caused by the formation of alkali- or alkaline earth-metal benzoates which are thermochemically more stable than benzoic acid which leads to inhibition of decomposition to CO<sub>2</sub> and benzene over NiO-Fe<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O.<sup>4</sup>

**Table 1** Effect of added alkali- and alkaline earth-metal oxides on conversion and selectivity<sup>a</sup> of benzoic acid to phenol

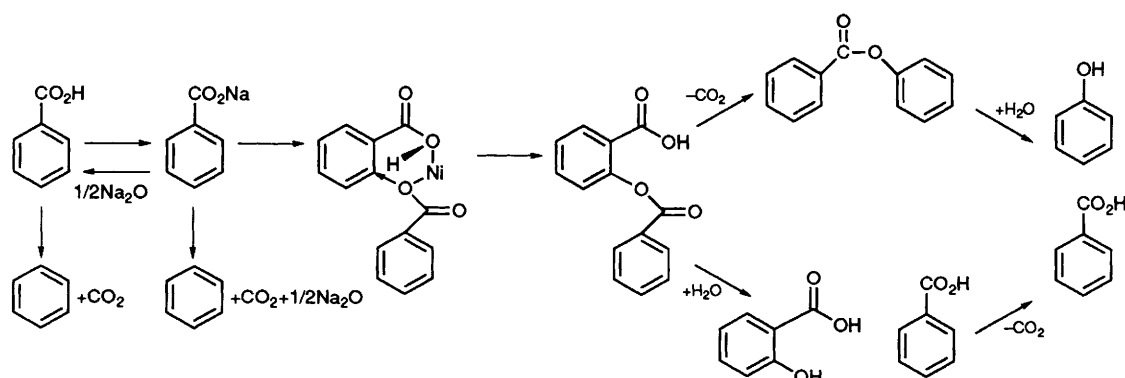
Additive <sup>b</sup>	Conversion (%)	Selectivity <sup>d</sup> (%)			STY/g (l cat) <sup>-1</sup> h <sup>-1</sup>
		Phenol	Benzene	CO + CO <sub>2</sub>	
None <sup>c</sup>	100	93.0	5.0	1.0	85
None	28.7	70.4	18.3	1.5	384
Na <sub>2</sub> O	100	91.1	7.8	1.9	1305
K <sub>2</sub> O	40.4	90.1	5.4	1.3	550
CaO	15.4	98.7	1.2	Trace	448
MgO	3.9	87.1	8.1	3.4	69

<sup>a</sup> Catalysts: 47.5% m/m NiO–51.5% m/m Fe<sub>2</sub>O<sub>3</sub>–1% m/m additive; prepared by coprecipitation, calcined at 800 °C; reaction conditions, benzoic acid–air–steam = 1:5:15 (molar ratio); space velocity = 10 000 h<sup>-1</sup>; reaction temperature = 400 °C. <sup>b</sup> Impregnated with aqueous solution of metal nitrates or carbonates. <sup>c</sup> Space velocity = 1600 h<sup>-1</sup>. <sup>d</sup> Selectivity is calculated on the basis of number of moles of benzoic acid converted.

**Table 2** Effect of Na<sub>2</sub>O content on catalytic activities<sup>a</sup>

Na <sub>2</sub> O content <sup>b</sup> (wt %)	Conversion (%)	Selectivity <sup>c</sup> (%)			STY/g (l cat) <sup>-1</sup> h <sup>-1</sup>
		Phenol	Benzene	CO + CO <sub>2</sub>	
0.5	95.2	90.1	7.6	1.9	2112
1.0	73.5	83.1	11.9	2.9	1352
2.0	70.1	60.3	37.7	1.1	1174
5.0	39.7	28.9	60.2	7.6	274

<sup>a</sup> Catalysts: Fe : Ni = 1 : 1 (atomic ratio); prepared by coprecipitation, calcined at 800 °C, reaction conditions, benzoic acid–air–steam = 1:4:10 (molar ratio); space velocity = 7700 h<sup>-1</sup>; reaction temperature = 400 °C; <sup>b</sup> Impregnated with aqueous solution of metal nitrate or carbonate. <sup>c</sup> Selectivity is calculated on the basis of the number of moles of benzoic acid converted.



**Fig. 1** The mechanism of phenol production over NiO-Fe<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O catalyst

Table 3 Vapour phase oxidation of toluic acid to cresol<sup>a</sup>

Toluic acid	Conversion (%)	Selectivity <sup>b</sup> (%)				
		<i>o</i> -Cresol	<i>m</i> -Cresol	<i>p</i> -Cresol	Phenol	CO + CO <sub>2</sub>
<i>o</i> -Toluic acid	73.4	Trace	9.1	0	23.1	2.1
<i>m</i> -Toluic acid	23.1	9.4	Trace	0.9	19.3	3.4

<sup>a</sup> Catalysts: 47.5% m/m NiO–51.5% m/m Fe<sub>2</sub>O<sub>3</sub>–1% m/m Na<sub>2</sub>O, prepared by coprecipitation, calcined at 800 °C; reaction conditions, toluic acid–toluene–air–N<sub>2</sub>–steam = 1:26:10:51 (molar ratio); space velocity = 3000 h<sup>-1</sup>. <sup>b</sup> Selectivity is calculated on the basis of number of moles of benzoic acid converted.

Table 2 shows the effect of Na<sub>2</sub>O content on the catalytic activity. The activity was measured after 10 h of continuous gas flow from the initial feed of benzoic acid. Both conversion and phenol selectivity decreased while benzene selectivity increased rapidly with increasing Na<sub>2</sub>O content. Thermal analysis of the catalysts, after measurement of activity, shows that the amount of sodium benzoate deposited on the catalyst surface increased with an increase in the Na<sub>2</sub>O content of the catalyst. These results suggest that the decrease in conversion with increasing Na<sub>2</sub>O content is due to accumulation of sodium benzoate which covers the active sites on the catalyst surface. It is presumed that the decrease in phenol selectivity and the increase in benzene selectivity with increasing Na<sub>2</sub>O content results from the decomposition of sodium benzoate which accumulates over time on the catalyst surface.

In order to confirm the reaction mechanism proposed, toluic acids were also employed, and the results are given in Table 3. *m*-Cresol from *o*-toluic acid and *p*- or *o*-cresol from *m*-toluic acid were obtained over the NiO–Fe<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O catalyst. These results indicate that hydrogen in the *o*-position

of the carboxylic group is substituted by OH and this supports the mechanism of oxidation of benzoic acid to phenol over NiO–Fe<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O as shown in Fig. 1.

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