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Oxidation of Benzoic Acid to Phenol in the Vapor Phase

II. Copper Catalysts

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The paper describes catalysts which have been screened for the vapor-phase oxidation of benzoic acid to phenol. The most active and selective are copper-containing catalysts promoted by other metals and supported on alumina. The best catalysts are Cu–Bi–Cd–Al_2O_3 and Cu–Bi–Pb–Al_2O_3 which produce phenol with 84% selectivity and with a conversion of benzoic acid of 33 and 52%, respectively. The proposed function of the metal promoters is to modify those surface features of copper catalysts which influence the rate of phenyl benzoate hydrolysis. This step determines the selectivity of phenol formation. © 1989 Academic Press, Inc.

INTRODUCTION

In a previous paper Part I (*1*), we described the effects of technological parameters on the selectivity of the vapor-phase oxidation of benzoic acid to phenol over a copper catalyst supported on alumina. Cupric benzoate was recognized as the key intermediate formed on the catalyst surface. The rate of cupric benzoate formation was found to determine the overall rate of benzoic acid oxidation.

In recent years the majority of work in the field of vapor-phase oxidation of benzoic acid to phenol has concerned the development of catalysts. All the catalysts described in the patent literature, as previously summarized (*1*), contain copper in combination with other metals. In the search for selective catalysts, we describe in the present paper the effects of support, promoters, and activators on the activity, selectivity, and life of copper catalysts in order to find the best composition for phenol formation.

EXPERIMENTAL

Catalysts. The metal catalysts supported on various carriers were prepared by the following procedures. Catalysts of types Cu–M_1–carrier and Cu–PcM_2–Al_2O_3, where M_1 is a metal of Group Ia or Group IIa of the periodic table and PcM_2 is the phthalocyanine of a transition metal, were prepared by impregnation of alumina or SiO_2 (1.0–1.6-mm particle size) with aqueous or pyridine solutions of various metal compounds according to the method described previously (*1*). After drying, they were calcined for 3.5 h at the temperatures given in Table 1 for the particular promoters chosen.

Catalysts supported on powdered aluminosilicates were prepared similarly; after evaporation of water the catalysts were mixed with γ-alumina (20 wt%), pelletized, and after gradual calcination to 500°C for 5 h were crushed to a particle size of 1.0–1.6 mm. Catalysts Cu–M_2–M_1–Al_2O_3, Cu–Bi–M_1–Al_2O_3, and Cu–Bi–M_2–Al_2O_3, where M_2 is a transition or other metal, were prepared by impregnation (24 h) of alumina (1.0–1.6 mm) with an aqueous solution of $Cu(NO_3)_2$. After evaporation of water, drying, and calcination at 750°C for 2 h, the catalyst was impregnated (24 h) with a salt of the metal M_2, and after drying again was calcined for 3.5 h at the temperatures given

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TABLE 1

Calcination Temperature of Cu–M_1–Al_2O_3

Promoter M_1	Li	Na	K	Ca	Mg	Ba	Sr
Temperature (°C)	710	500	500	610	700	510	870

in Table 2 for the particular metals indicated. Some catalysts were further impregnated (24 h) by aqueous solution of the hydroxide of metal M_1, and after evaporation of water and drying they were calcined at 500°C for 11 h. Aluminas with different surface areas were prepared by calcination of γ-alumina at various temperatures.

Procedure. All catalysts were tested by the method described previously (*1*) in a tubular fixed-bed reactor filled with 47–50 g of a catalyst. The same procedure as before was also used for the analysis of reaction products and the physicochemical investigation of the catalysts. The tables summarize the data obtained after runs of 5–7 h duration.

RESULTS

Various metal catalysts were tested for the oxidation of benzoic acid to phenol. This section summarizes the results obtained with copper-based catalysts. At first, we investigated the effect of the support material on the catalytic activity of CuO promoted by potassium oxide. Initial screening showed (Table 3) that a variety of traditional supports such as silica and aluminosilicates are poor catalyst carriers. The catalysts deposited on these carriers possess low activity and selectivity and rapidly deactivate. Good results were obtained with low-surface-area aluminas prepared by thermal treatment. This indicates that surface features may play a significant role in the oxidation process. Benzene used as solvent is stable under the experimental conditions employed and is not oxidized.

TABLE 2

Calcination Temperature of Cu–Bi–$M_1/M_2/$–Al_2O_3 and Cu–$M_1/M_2/$–Al_2O_3

Metal M_2	Fe	Co	Ni	Cr	Cd	Mn
Temperature (°C)	700	370	710	370	660	750
Metal M_2	Bi	Zn	Mo	V	Pb	
Temperature (°C)	570	620	650	390	650	

From Part I (*1*) it is clear that the rate of reoxidation of Cu(I) to Cu(II) benzoate on the catalyst surface determines the overall rate of the reaction. In an effort to increase this rate, catalysts with a higher content of CuO were prepared. As is seen from Table 4, the catalytic activity is influenced not only by the amount of CuO deposited on the support but also by the type and the concentration of the promoter. However, in both cases an optimal concentration exists. In order to compare the promoting effect of various metals of Groups Ia and IIa, catalysts were tested under comparable conditions during runs over several hours (Table 5). The best results were obtained with copper catalysts promoted by lithium. Thus, at 95% conversion of benzoic acid, phenol is produced with 44.3 mol% yield and, moreover, the catalytic activity is almost unchanged during a 15-h run. Other metals listed in Table 5 also increase the selectivity of phenol formation; however, both conversion of benzoic acid and life of the catalyst are lower. Catalysts promoted by magnesium and calcium rapidly deactivate, whilst those with barium and sodium deactivate more slowly. For instance, Cu–Ca–Al_2O_3 catalyst after a 14-h reaction cycle loses about 75% of its activity. Moreover, it is of interest to note that with Cu–Ba–Al_2O_3 catalyst an "induction period" of about 9 h is needed to reach steady-state conversion and product formation. With other catalysts this period is about 2–4 h.

Investigation of the influence of a number of transition metals on the activity of Cu–

TABLE 3

Effect of CuO (10 wt%) + K_2O (10 wt%) Oxides Supported on Various Carriers

Support	Surface area (m^2 g^{-1})	Mean diameter of pores (nm)	Conversion (%)	Yield (mol%)		r_{CO_2} (l h^{-1} kg_{cat}^{-1})
				PhOH	DP + DPO	
Alumina	159	3.61	100	10.1	3.0	15.8
	145	4.18	97	9.7	2.3	24.3
	141	4.30	98	11.2	2.2	20.8
	131	4.29	100	17.0	4.0	21.0
	120	4.38	100	20.1	14.8	21.6
	116	4.55	100	26.1	12.2	22.8
	103	4.65	75	22.9	13.9	9.4
	5	—	30	Traces	Traces	0.5
Bentonite	64	1.93	~50	8.1	2.9	22.0
Mordenite	—	—	~40	~8	0.6	21.5
Erionite	376	0.87	~50	3.4	~0.1	19.8
Silica	212	—	10	2.0	0	1.1

Note. Conditions: 300°C; 1 atm; BzOH, 0.057 kg h^{-1} kg_{cat}^{-1}; benzene, 1.10 kg h^{-1} kg_{cat}^{-1}; H_2O, 0.50 kg h^{-1} kg_{cat}^{-1}; O_2 flow, 21.3 l h^{-1} kg_{cat}^{-1}. PhOH indicates phenol; DP, diphenyl; DPO, diphenyloxide; r_{CO_2}, rate of CO_2 formation.

M_2–K–Al_2O_3-type catalyst shows (Table 6) that for the most part they act negatively. Besides decreasing benzoic acid conversion, the decarboxylation reaction is markedly increased, this being usually accompanied by production of a large amount of carbon dioxide and obviously of benzene. This is typical for catalysts doped with Zn, Bi, Mo, and Ni. The improvement of selectivity to phenol formation was observed only in the presence of lead oxide but at lower conversion of benzoic acid. In addi-

TABLE 4

Effect of Catalyst and Promoter Loading

Catalyst (wt% CuO)	Promoter (wt%)		Conversion (%)	Yield (mol%)		r_{CO_2} (l h^{-1} kg_{cat}^{-1})
	K_2O	Li_2O		PhOH	DP + DPO	
10	0		55	11.0	1.5	9.8
	5		100	22.1	15.0	11.2
	10		100	26.1	12.2	22.8
	20		90	11.2	4.0	21.4
		10	95	44.3	2.5	11.7
		10[a]	50	42.0	2.0	6.1
		15	52	37.2	4.1	4.7
10[b]	10		100	17.0	4.0	21.0
20[b]	10		83	25.9	9.8	12.9
30[b]	10		78	12.3	5.3	18.2

Note. Conditions as in Table 3. Carrier: alumina with surface area 116 m^2 g^{-1}.

[a] Alumina, 103 m^2 g^{-1}.

[b] Alumina, 131 m^2 g^{-1}.

TABLE 5

Effect of Promoters

Promoter	Conversion (%)	Yield (mol%)		r_{CO_2} (l h^{-1} kg$_{cat}^{-1}$)
		PhOH	DP + DPO	
—	~45	11.0	1.5	9.8
Li_2O	95	44.3	2.5	11.7
Na_2O	54	21.2	3.3	9.6
K_2O	100	26.1	12.2	22.8
MgO	30	15.0	2.1	4.3
CaO	37	14.2	1.0	3.2
BaO	74	18.9	5.9	8.7
SrO[a]	35	21.0	3.4	5.5

Note. Conditions as in Table 3. Catalyst: 10 wt% CuO + 10 wt% promoter (as oxide) on 116 m^2 g^{-1} alumina.

[a] At 285°C.

tion to this we observed that the effect of transition metals on the activity of copper catalyst is very sensitive to the type of alkali metal promoter and the method of catalyst preparation. The results summarized in Table 6 indicate that the Li_2O promoter is more efficient in improving the selectivity of mixed-metal catalysts than K_2O; the phenol yield increases and the rate of carbon dioxide formation decreases. Catalysts combined with two transition metals, type Cu–M_2–K–Al_2O_3, prepared by simultaneous impregnation and calcination of mixtures of metal salts, are very nonselective for the oxidation of benzoic acid to phenol. The commercial Cu–Cr–Zn oxide catalyst is also very poor in activity.

TABLE 6

Effect of Activators

Activator	Conversion (%)	Yield mol%		r_{CO_2} l h^{-1} kg$_{cat}^{-1}$
		PhOH	DP + DPO	
—	100	26.1	12.2	22.8
Fe	100	15.9	20.1	27.3
Fe[a]	100	1.1	3.5	28.6
Co	80	20.0	9.1	15.9
Ni	100	2.9	14.8	28.3
Mn	67	13.5	2.0	17.5
Mn[b]	62	20.0	0.8	13.6
Cr	87	20.8	9.9	14.3
Cr[a]	100	5.9	4.2	21.8
Mo	92	22.2	0.8	21.6
V	78	17.3	3.2	20.5
Bi	50	13.1	3.0	18.9
Bi[b]	70	40.0	5.9	6.5
Pb	60	38.0	6.1	10.3
Pb[b]	85	52.5	8.0	10.6
Zn	75	12.2	1.7	18.5
Cd	90	6.9	1.0	25.2
Cu–Cr–Zn[c]	30	0	0	—

Note. Conditions as in Table 3. Catalyst: 10 wt% CuO + 10 wt% activator (as oxide) + 10 wt% K_2O on 116 m^2 g^{-1} alumina.

[a] Catalyst prepared by simultaneous impregnation and calcination with mixed Cu–M_2 metal salts.

[b] Instead of K_2O, promoter was Li_2O.

[c] Catalyst 9.1 wt% CuO + 21.6 wt% Cr_2O_3 + 58.9 wt% ZnO.

TABLE 7

Activity of Cu–Bi–Al_2O_3 Catalyst Doped with Various Metals

Metal	Conversion (%)	Yield (mol%)		r_{CO_2} (l h^{-1} kg$_{cat}^{-1}$)
		PhOH	DP + DPO	
Li	70	40.0	5.9	6.5
K	50	13.1	3.0	18.9
Cd	33	27.9	4.5	11.2
Mo	70	40.5	4.1	21.8
Pb	52	43.2	7.0	5.4

Note. Conditions as in Table 3. Catalyst: 10 wt% CuO + 10 wt% Bi_2O_3 + 10 wt% metal oxide on 116 m^2 g^{-1} alumina.

The minimum rate of carbon dioxide formation with high selectivity of phenol formation was obtained with Cu–Bi–Li–Al_2O_3 and Cu–Pb–Li–Al_2O_3 catalysts. Attempts to modify these catalysts resulted in a further improvement in the selectivity of phenol formation (Table 7). Under the experimental conditions considered the most selective catalysts are Cu–Bi–Cd–Al_2O_3 and Cu–Bi–Pb–Al_2o_3 which produce phenol with about 84% selectivity and a low rate of CO_2 formation. However, the latter catalyst is the more active and operates with a higher conversion of benzoic acid.

The effect of some of the transition metals investigated above was also tested in the form of their highly thermostable phthalocyanines. As is seen from Table 8, such catalysts are usually more selective but their catalytic activity is lower, thereby leading to a decrease in benzoic acid conversion. The lower activity of all Cu–PcM–Al_2O_3 catalysts may be attributed to their method of preparation using pyridine solu-

TABLE 8

Activity of Copper Catalysts Doped with Metal Phthalocyanines

Phthalocyanine	Conversion (%)	Yield (mol%)		r_{CO_2} ($l\ h^{-1}\ kg_{cat}^{-1}$)
		PhOH	DP + DPO	
—[a]	53	6.2	1.0	4.8
Cu	22	14.2	2.1	1.9
Cu[b]	50	22.1	5.0	16.1
Cr	30	13.9	4.0	5.6
Co	22	9.8	1.5	6.2
Fe	20	9.1	1.7	9.5
Mn	21	1.0	1.9	3.2
Bi[c]	67	7.9	2.7	—
Mo[c]	90	20.5	2.8	17.6
W	52	1.2	0.1	11.0

Note. Conditions as in Table 3. Catalyst: 10 wt% CuO + 10 wt% PcM on 116 $m^2\ g^{-1}$ alumina.

[a] Catalyst washed with pyridine and then dried.

[b] Promoter, 10 wt% K_2O

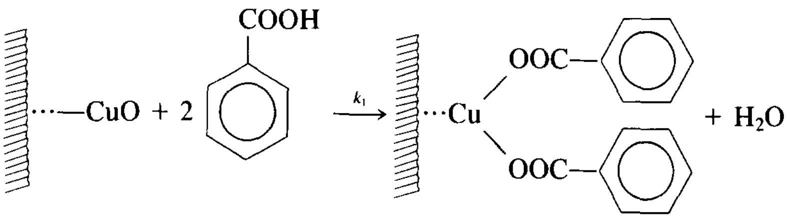
[c] At 285°C.

tion of metal phthalocyanines. Thus, washing the catalysts with pyridine always results in a decrease in their activity (Tables 6 and 8).

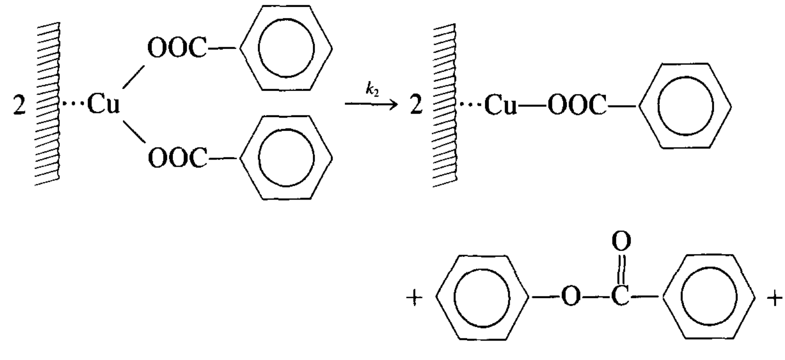
DISCUSSION

Several copper catalysts doped with other metals are effective for the selective vapor-phase oxidation of benzoic acid to phenol. As regards the carrier, it seems to be important to have alumina with a defined surface area (~120 $m^2\ g^{-1}$). Other aluminas, SiO_2, and amorphous or crystalline aluminosilicates are less suitable carriers. Although we have not specifically studied the relation between the metal catalyst and the type of support, the results obtained indicate that both the combination of the metals and the method of catalyst preparation are extremely crucial for obtaining a good catalyst.

Mechanistic studies of the vapor-phase oxidation of benzoic acid [reactions (1)–(5) below] led to the suggestion (*1*) that the rate of reoxidation of Cu(I) to Cu(II) benzoate on the catalyst surface is the rate-determining step (reaction 4).



(1)



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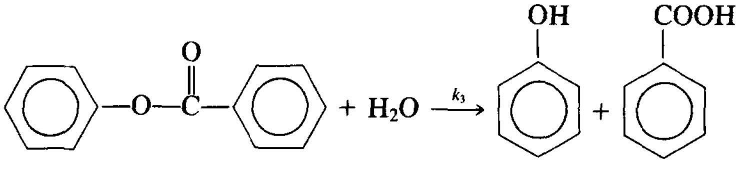

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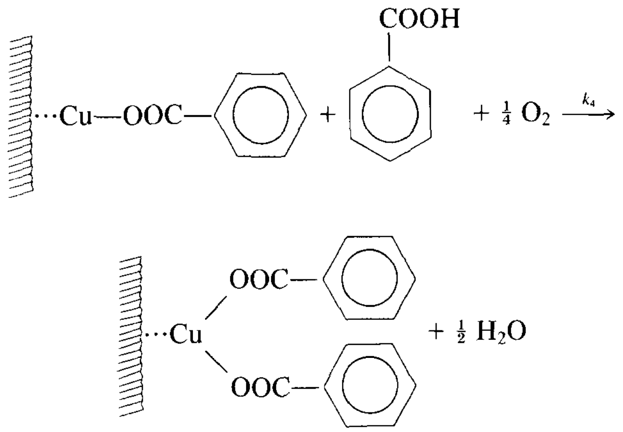

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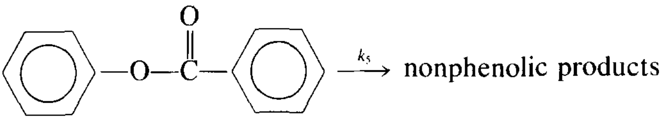

(5)

In the commercial liquid-phase process of benzoic acid oxidation, the selectivity of cupric benzoate catalyst is improved by the presence of magnesium benzoate which catalyzes the hydrolysis of phenyl benzoate (*2*). Attempts to enhance this reaction step also in the vapor phase were made by impregnation of the alumina support by various metal promoters. This procedure leads to a decrease in the surface area of the catalysts to about 35–55 $m^2\ g^{-1}$ and a modification of the surface constitution of alumina. As revealed by X-ray diffraction, the Cu–Li–Al_2O_3 catalyst has a morphology corresponding to that of the lithium aluminates (*3*); however, the content of the CuO phase on the catalyst surface remains unchanged. This is an indication that the surface features and their acid–base properties (Table 3; Ref. (*4*)) influence the rate of phenyl benzoate hydrolysis.

From the kinetic data obtained in solution at 100°C it is evident (*5*) that the rate of base-catalyzed hydrolysis of phenyl benzoate is several orders higher than that of acid-catalyzed hydrolysis. Also, in the vapor-phase oxidation of benzoic acid, higher selectivities were always observed with catalysts promoted by metals of Groups Ia and IIa, i.e., catalysts possessing basic properties. The basicity of the investigated catalysts was determined semiquantitatively by the pulse technique using acetic acid and benzoic acid according to the method described by Ai (*6*).

The fact that catalysts possessing basic properties are more selective for oxidation of benzoic acid to phenol supports the experiments on phenyl benzoate hydrolysis. As is seen from Table 9, the hydrolysis is favored over the more basic Cu–Pb–Li–Al_2O_3 catalyst than over the less basic Cu–K–Al_2O_3 or copper-free K–Al_2O_3 catalysts. The yield of phenol higher than theory obtained over Cu–Pb–Li–Al_2O_3 catalyst (119.0 mol%) indicates that also in the absence of oxygen, the benzoic acid formed by the hydrolysis of phenyl benzoate is oxidized to phenol via reaction steps 1–3. The subsequent oxidation is obvious over both catalysts in the presence of oxygen, as proved by the absence of benzoic acid in the outlet from the reactor. Experiments summarized in Table 9 also suggest that Reaction 5 is not a simple thermal decomposition of phenyl benzoate, but that it is probably induced by the copper catalyst which plays a significant role in this process.

TABLE 9

Reaction of Phenylbenzoate (PhOBz) at 285°C and 1 atm over Catalysts with Different Basicities

Catalyst	Feed to the reactor (kg h^{-1} kg$_{cat}^{-1}$)				Conversion of PhOBz (%)	Yield (in mol%)[b]		
	Benzene	PhOBz	H_2O	Oxygen[a]		PhOH	DP + DPO	BzOH
$Cu-Pb-Li-Al_2O_3$	1.10	0.029	0.50	21.3	100	185.0	1.9	0
	1.10	0.029	0.50	0	97	119.0	0.1	61.0
	1.10	0.029	0	0	33	18.6	Traces	Traces
	1.10	0.029	0	21.3	98	55.0	2.3	0
$Cu-K-Al_2O_3$	1.10	0.029	0.50	21.3	100	137.7	2.5	0
	1.10	0.029	0.50	0	69	59.7	0.1	72.3
	1.10	0.029	0	21.3	100	29.0	1.0	0
$K-Al_2O_3$[c]	1.10	0.029	0.50	21.3	45	26.4	—	43.9

[a] In l h^{-1} kg$_{cat}^{-1}$.

[b] Assuming 1 mol each of PhOH, DP + DPO, and BzOH per mol PhOBz.

[c] Catalyst without copper.

Less probable is the suggestion that benzoates of metals of Group Ia or IIa are predominantly formed on the catalyst surface because their decomposition relative to cupric benzoate is always nonselective (*7*, *8*). The thermal stability of these salts increases in the following order of metal cations (*9*), Rb > K > Na > Li, which does not correlate with the observed selectivity of the oxidation (Table 5). The same assumption is probably true in the case of catalysts doped with various transition metals (Table 6). Therefore, the change in activity of this type of catalyst is caused by the competitive reactivity of the corresponding metal oxides with benzoic acid followed by a rapid decomposition of the metal benzoates formed at the reaction temperature. This fact is underlined, for example, by the experiments on the thermal decomposition of nickel benzoate at 400°C showing that per mole of salt decomposed 0.41 mol of phenol is produced (*10*). Over nickel-doped $Cu-Ni-K-Al_2O_3$ catalyst, however, only a minor amount of phenol is formed (Table 6). X-ray analysis of the mixed-metal catalysts $Cu-M_2-M_1-Al_2O_3$ does not confirm the formation of a mixed-metal oxide phase, e.g., a spinel structure on the catalyst surface. This is reasonable, since the catalysts mentioned were prepared by a two-stage impregnation and calcination and the formation of such phases by this method is less probable. Transition metals bound in the phthalocyanine ring, i.e., complexes which under the reaction temperature of about 300°C are thermally stable (*11*) and formation of metal benzoates from them is hindered, also influences the selectivity of the oxidation. However, in this case the lower activity of the catalyst is probably caused by the different method of catalyst preparation.

As a result of this work we have found that the best catalysts for the vapor-phase oxidation of benzoic acid to phenol are Cu–Bi oxides doped with Li, Cd, or Pb oxides supported on a γ-alumina with a surface area of about 120 m^2 g^{-1}. The promoting influence of the metals studied on the activity of copper catalysts can be interpreted by assuming that the major importance for the selectivity of phenol formation is held by the rate of phenyl benzoate hydrolysis which depends on the surface constituents of the catalyst.

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