JOURNAL OF CATALYSIS **155**, 158–162 (1995)

NOTE

Liquid–Phase Benzene Oxidation to Phenol with Molecular Oxygen Catalyzed by Cu-Zeolites

The oxidation of benzene to form phenol using cuprous chloride as a catalyst has been reported by Sasaki and his co-workers (1, 2), who used reaction system oxygen molecules as the oxidant. Takehira and his co-workers have studied benzene oxidation with molecular oxygen catalyzed by Cu(II) salts in the presence of ascorbic acid (3). Cu ion-exchanged zeolites have been reported to be useful as catalysts for the gas-phase oxidation of some organic materials (4, 5), and copper ions in zeolites have been indicated to have redox properties according to physicochemical measurements (6–12). Armed with this knowledge, we have tried the liquid–phase oxidation of benzene with molecular oxygen under atmospheric pressure at room temperature using Cu ion-exchanged zeolite catalysts in the presence of ascorbic acid as a reducing reagent for Cu ions. The catalytic behavior of the Cu zeolites for the benzene oxidation was compared with that of nonanchored cupric and cuprous chloride catalysts. Also, some Cu catalysts impregnated on some amorphous oxide supports, in addition to the zeolites, were tested as catalysts for benzene oxidation with molecular oxygen.

NaZSM-5 zeolite (Si/Al atomic ratio 35), designated NaZ, was prepared according to the method in the patent (17). NaY zeolite (Si/Al atomic ratio 2.8), NaX zeolite (Si/Al atomic ratio, 1.4), and KL zeolite (Si/Al atomic ratio, 3.4) were obtained from Toso Company. Mordenite (Zeolon; Si/Al atomic ratio 7.2) was purchased from Norton. SiO_2 was Davison grade 62. γ-Al_2O_3 (JRC–ALO-4), SiO_2–Al_2O_3 (JRC–SAH-1), and TiO_2 (JRC–TiO-4) were all reference catalysts from Japan Catalysis Society. The H-type zeolites were prepared by ion exchanging the corresponding parent Na-type zeolites three times with an aqueous solution of 1 mole/liter on NH_4Cl at 353 K for 6 h, followed by filtration, washing with deionized water, drying at 393 K overnight, and calcination at 773 K for 5 h in air. The Cu ion-exchanged zeolites were prepared by ion exchanging each parent zeolite with an aqueous solution of $Cu(CH_3COO)_2$ followed by filtration, washing with deionized water, drying at 393 K overnight, and calcination at 773 K for 5 h in air. The Si/Al ratios of the ZSM-5 zeolites synthesized in this study and the degree of the Cu ion exchange of each Cu zeolite were determined by dissolving these zeolites with hydrogen fluoride and measuring the resulting diluted aqueous solution using atomic absorption equipment. The Cu ion-exchanged SiO_2 was prepared as follows: the SiO_2 support (Davison Grade 62) was ion exchanged with $Cu(NO_3)_2 \cdot 2H_2O$ which was maintained at pH 8–9 at 358 K for 2 h, filtered, washed and deionized water, dried at 393 K overnight, and calcined at 773 K for 5 h in air. The oxide-supported Cu catalysts were prepared by impregnating with $CuCl_2$, drying at 393 K overnight, and calcining at 773 K for 5 h in air. The liquid-phase oxidations of benzene were carried out in a 50 cm^3 round-bottomed flask immersed in a thermostated water bath, which was usually maintained at 303 K, under an oxygen atmosphere (1 atm). Into benzene (2 cm^3, 22.5 mmol) in 20 cm^3 of solvent, the correct amounts of catalyst and ascorbic acid were added. The resulting heterogeneous solution was stirred with a magnetic stirrer for the prescribed time (usually 24 h). The reaction products were analyzed by a gas chromatograph using a 3-m stainless steel column (3 mm diameter) filled with silicon OV-17/Chromosorb GAW DMCS (473 K; carrier gas, 30 cm^3/min N_2) and using 2-propanol as an internal standard.

The main product of benzene oxidation with molecular oxygen was phenol, irrespective of the supports when using the Cu ion-exchanged zeolites and Cu-impregnated oxides as catalysts. The zeolite supports themselves were found to have no catalytic activity for the benzene oxidation. Also it was found that no oxidation of benzene occurred using the Cu ion-exchanged zeolites under a nitrogen atmosphere in place of an oxygen atmosphere.

To compare the oxidation activity for the liquid-phase benzene oxidation to form phenol with the corresponding supported Cu catalysts, some copper salts, which were not anchored on the supports, were tested as catalysts in

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TABLE 1

Benzene Oxidation with O_2 Catalyzed by Cu Salts[a]

Catalyst	Solvent	Ascorbic acid (mmol)	Phenol[b] (mmol)	Phenol/Cu[c]
$CuCl_2$	H_2O	0	0	0
		4	0.10	0.025
	1 *N* CH_3COOH aq. sol.	0	0	0
		4	0.12	0.030
$Cu(CH_3COO)_2$	H_2O	0	0	0
		4	0.12	0.030
	1 *N* CH_3COOH aq. sol.	0	0	0
		4	0.15	0.038
$Cu(NO_3)_2$	H_2O	0	0	0
		4	0.09	0.022
	1 *N* CH_3COOH aq. sol.	0	0	0
		4	0.10	0.025
$CuSO_4$	H_2O	0	0	0
		4	0.10	0.025
	1 *N* CH_3COOH aq. sol.	0	0	0
		4	0.12	0.030

[a] Catalyst, 4 mmol; benzene, 2 cm_3 (22.5 mmol); temperature, 303 K; time, 24 h.

[b] The amount of phenol produced.

[c] (The phenol produced/the amount of Cu in the catalyst) mole ratio.

both water and 1 mol/liter acetic acid aqueous solvents, with the results shown in Table 1. No benzene was produced without ascorbic acid, irrespective of the copper salts used here. However, phenol was obtained using ascorbic acid as a reducing reagent for Cu ions, though the amounts of phenol produced were considerably low. The mole ratios of the phenol produced to the Cu ion are considerably less than unity for all the Cu salts used here as catalysts.

The Cu catalyst supported on the oxides was found to have catalytic activity for benzene oxidation in the presence of ascorbic acid (Table 2). The mole ratios of phenol obtained to the Cu ion on the catalyst were larger than unity, in contrast with the results with the nonanchored Cu catalytic systems shown in Table 1. The Cu species supported on oxides is thus considered to be more effectively used for phenol formation, rather than nonanchored Cu species such as $CuCl_2$. Also, the oxide supported Cu catalysts in the aqueous solvent including acetic acid were again found to have larger oxidation

TABLE 2

Oxidation of Benzene with O_2 Catalyzed by Cu Supported on Oxides[a]

Catalyst	Cu impregnated		Solvent	Phenol[b] (mmol)	Phenol/Cu[c]
	(wt %)	(mmol $\times 10^2$)			
Cu/SiO_2	1.3	8.67	H_2O	0.11	1.27
			1 *N* CH_3COOH aq. sol.	0.16	1.85
Cu/SiO_2[d]	1.1	8.85	H_2O	0.10	1.13
			1 *N* CH_3COOH aq. sol.	0.15	1.69
Cu/Al_2O_3	1.6	10.61	H_2O	0.20	1.89
			1 *N* CH_3COOH aq. sol.	0.36	3.39
$Cu/SiO_2–Al_2O_3$	1.3	8.64	H_2O	0.18	2.08
			1 *N* CH_3COOH aq. sol.	0.26	3.01
Cu/TiO_2	1.1	7.30	H_2O	0.13	1.78
			1 *N* CH_3COOH aq. sol.	0.14	1.92

[a] Catalyst, 0.4 g; ascorbic acid, 4 mmol; benzene, 2 cm_3 (22.5 mmol); temperature, 303 K; time, 24 h.

[b] The amount of phenol produced.

[c] (The phenol produced/the amount of Cu in the catalyst) mole ratio.

[d] Prepared by the ion-exchange method.

TABLE 3

Oxidation of Benzene with O_2 Catalyzed by Cu Ion-Exchanged Zeolites[a]

Catalyst	Cu ion-exchanged (%)	Cu ion-exchanged (mmol $\times 10^2$)	Solvent	Phenol[b] (mmol)	Phenol/Cu[c]
Cu-NaZ	67	5.79	H_2O	0.07	1.21
			1 *N* CH_3COOH aq. sol.	0.13	2.24
Cu-HZ	67	5.90	H_2O	0.08	1.36
			1 *N* CH_3COOH aq. sol.	0.17	2.88
Cu-NaY	9.5	5.09	H_2O	0.26	5.10
			1 *N* CH_3COOH aq. sol.	0.38	7.47
Cu-HY	9.5	5.72	H_2O	0.21	3.68
			1 *N* CH_3COOH aq. sol.	0.27	4.72
Cu-NaX	14	4.46	H_2O	0.21	4.71
			1 *N* CH_3COOH aq. sol.	0.32	7.17
Cu-HX	14	4.47	H_2O	0.13	2.91
			1 *N* CH_3COOH aq. sol.	0.21	4.70
Cu-KL	7.8	5.71	H_2O	0.19	3.33
			1 *N* CH_3COOH aq. sol.	0.27	4.73
Cu-Mordenite	23	9.85	H_2O	0.25	2.54
			1 *N* CH_3COOH aq. sol.	0.32	3.25

[a] Catalyst, 0.4 g; ascorbic acid, 4 mmol; benzene, 2 cm^3 (22.5 mmol); temperature, 303 K; time, 24 h.
[b] The amount of phenol produced.
[c] (The phenol produced/the amount of Cu in the catalyst) mole ratio.

activities for benzene formation than the corresponding ones in pure water solvent.

The results of the oxidation of benzene with oxygen molecules using the Cu ion-exchanged zeolites in the presence of ascorbic acid are shown in Table 3. The Cu species ion exchanged on the zeolites were found to have greater activity for benzene formation than the nonanchored Cu species shown in Table 1. The Cu ions anchored on supports such as zeolites will tend to be isolated from each other and the reactant, benzene, will be able to more easily and efficiently access the isolated Cu ions which are present in a higher density state than the unsupported Cu ions in the solution; this is considered to be one of the reasons that it is more effective to use Cu ions anchored on supports as catalysts. Faujasite-type zeolites, such as Y and X types, among the zeolites studied here were particularly effective for the oxidation activity. It is evident that the Cu–Na-type zeolites have higher oxidation activities than the Cu–H-type zeolites, though the oxidation activities of both the proton and the sodium types of the ZSM-5 zeolite were not so different from each other. Among the alkali-type Cu zeolites, the order of the phenol/Cu mole ratios was Cu–NaY > Cu–NaX > Cu–KL > Cu–mordenite > Cu–NaZ, which is just the opposite of the order of the Si/Al atomic ratios of these zeolites. One of the factors which govern the benzene oxidation is thus considered to be the hydrophilicity of the zeolite used as the support. An ascorbic acid molecule as the reducing reagent for Cu ions will be able to easily enter into the pores of zeolites with high hydrophilicity such as faujasite-type zeolites and reduce the Cu ions in the zeolites. The pore structure of the zeolites will be considered as another factor which governs the benzene oxidation. Thus ascorbic acid, a reducing reagent for Cu ions, will be able to more easily enter the super-

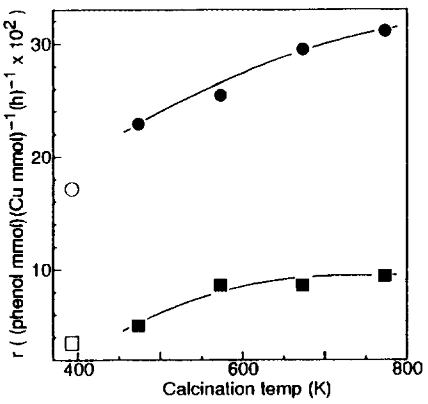

FIG. 1. Effect of calcination temperature on benzene oxidation. Benzene, 2 cm^3 (22.5 mmol); ascorbic acid, 4 mmol; solvent, 20 cm^3 acetic acid (1 mol/liter) aqueous solution; reaction temperature, 303 K; reaction time, 24 h; ●, 0.40 g Cu-NaY(9.5) (percentage of Cu ion exchange, 9.5%; Cu, 0.8 wt%); ■, 0.40 g Cu-NaZ(67) (Cu, 0.9 wt%); ○, 0.4 g Cu-NaY(9.5) dried at 393 K only; □, 0.4 g Cu-NaZ(67) dried at 393 K only.

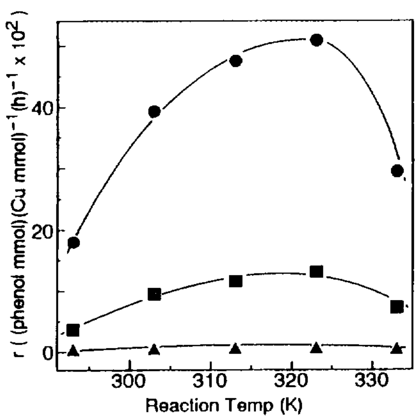

FIG. 2. Effect of reaction temperature on benzene oxidation. Benzene, 2 cm^3 (22.5 mmol); ascorbic acid, 4 mmol; solvent, 20 cm^3 acetic acid (1 mol/liter) aqueous solution; reaction temperature, 303 K; reaction time, 24 h; ▲, 0.53 g (4 mmol) $CuCl_2$; ●, 0.20 g Cu–NaY(9.5) (Cu, 0.8 wt%); ■, 0.4 g Cu–NaZ(67) (Cu, 0.9 wt%).

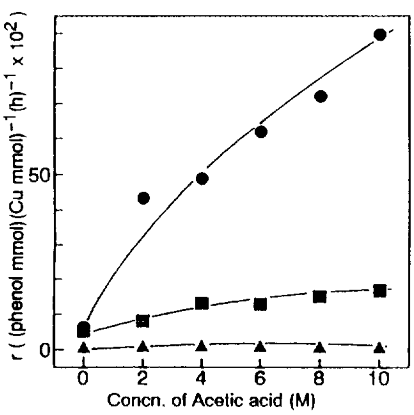

FIG. 3. Effect of concentration of acetic acid on benzene oxidation. Benzene, 2 cm^3 (22.5 mmol); ascorbic acid, 4 mmol; solvent, 20 cm^3 acetic acid (1 mol/liter) aqueous solution; reaction temperature, 303 K; reaction time, 24 h; ▲, 0.53 g (4 mmol) $CuCl_2$; ●, 0.20 g of Cu–NaY(9.5) (Cu, 0.8 wt%); ■, 0.4 g Cu–NaZ(67) (Cu, 0.9 wt%).

cage of faujasite-type zeolites such as *Y* and *X* zeolites and to access the Cu ions held in the supercage (4, 6, 9). Also the Cu zeolites in the aqueous solvent with acetic acid were found to have higher catalytic activity for the benzene oxidation than those in water solvent, irrespective of the type of zeolite. The catalytic behavior of the Cu ion-exchanged zeolites, particularly Cu–NaY and Cu–NaZ zeolites, for benzene oxidation is investigated in detail next.

The influence of calcination temperature of the zeolite on the rate per Cu ion (*r*, turnover frequency) is illustrated in Fig. 1 using Cu–NaZ and Cu–NaY zeolites. The results on the Cu zeolites dried at 373 K are also shown for comparison with those pretreated by calcination. The rate (*r*) increased calcination temperature until around 673 K and leveled off with further increase in the temperature, irrespective of the type of Cu zeolites used here.

The dependence of the rate (*r*) on the reaction temperature was investigated in the temperature range of 293 to 333 K using the Cu–NaZ, Cu–NaY, and nonanchored $CuCl_2$ catalysts (Fig. 2). The rates (*r*) of the Cu–NaZ and Cu–NaY were found to increase with increased reaction temperature and to pass through a maximum at ca. 323 K. A further increase in the reaction temperature caused decreases in the rates. One of the reasons for the decreased rate at higher reaction temperatures is considered to be a decrease in the solubility of oxygen molecules in the aqueous solvent at higher reaction temperatures. The decomposition of the hydrogen peroxide formed, which was detected in the aqueous solution with Cu–NaY catalyst and ascorbic acid under atmospheric O_2 (13), at a higher temperature will also cause retardation of the formation of phenol. The decrease in the hydroxy radical species generated from hydrogen peroxide is thus considered as one of the causes of the decrease in phenol formation at higher reaction temperatures.

The dependence of the phenol formation on the amount of acetic acid in the aqueous solvent was investigated using the Cu–NaZ, Cu–NaY, and nonanchored $CuCl_2$ (Fig. 3). The rate (*r*) catalyzed by the Cu–NaZ zeolite tended to be slightly promoted by an increase in the ascorbic acid concentration. The oxidation activity (*r*) of the Cu–NaY for phenol formation was found to

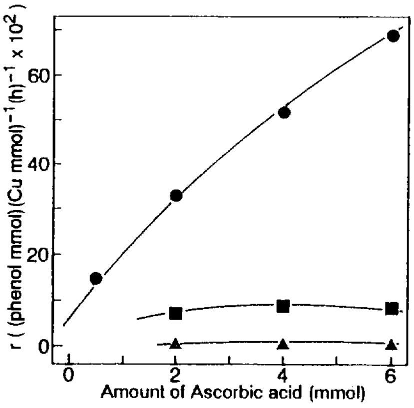

FIG. 4. Effect of amount of ascorbic acid on benzene oxidation. Benzene, 2 cm^3 (22.5 mmol); ascorbic acid, 4 mmol; solvent, 20 cm^3 of acetic acid (1 mol/liter) aqueous solution; reaction temperature, 303 K; reaction time, 24 h; ▲, 0.53 g (4 mmol) $CuCl_2$; ●, 0.20 g Cu–NaY(9.5) (Cu, 0.8 wt%); ■, 0.4 g Cu–NaZ(67) (Cu, 0.9 wt%).

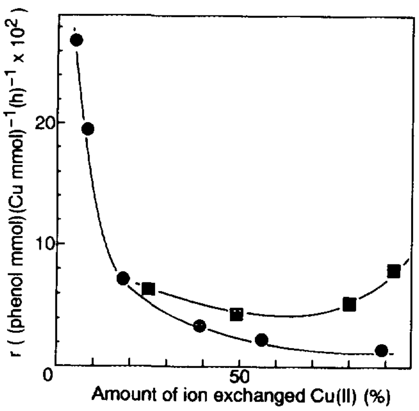

FIG. 5. Effect of percentage of Cu ion exchange on benzene oxidation. Benzene, 2 cm^3 (22.5 mmol); ascorbic acid, 4 mmol; solvent, 20 cm^3 water; reaction temperature, 303 K; reaction time, 24 h; ●, 0.4 g Cu–NaZ; ■, 0.2 g Cu–NaY.

appreciably increase with increased acetic acid concentration.

The influence of the ascorbic acid amount on the rate (*r*) is illustrated in Fig. 4 using Cu–NaZ, Cu–NaY, and nonanchored $CuCl_2$ as the catalyst. An increase in ascorbic acid with the Cu–NaZ catalyst caused an increase in the rate (*r*), but a further increase in ascorbic acid tended to decrease the rate. The rate (*r*) catalyzed by Cu–NaY was found to be profoundly promoted with an increase in the amount of the reducing reagent, ascorbic acid.

The variations in the rate (*r*) with the degree of Cu ion exchange are illustrated in Fig. 5 using Cu–NaZ and Cu–NaY zeolites in water solvent. The rate monotonically decreased with an increase in the degree of Cu ion exchange in the Cu–NaY zeolites. The increase in percentage of the Cu ion exchange of the Cu–NaZ zeolites caused a slight decrease in the rate up to around 70–80%. However, the rate tended to increase with a further increase in the percentage. The higher density of the Cu ions in the Cu–NaY in comparison with that in the Cu–NaZ may prevent their effective usage as active sites, since access of the reactant to the Cu ion becomes difficult with the increase in the percentage of ion-exchanged Cu.

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Received July 20, 1994

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