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Benzyl Alcohol Oxidation over Y-Type Zeolite Ion-Exchanged with Copper(II) Ion

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The vapor-phase oxidation of benzyl alcohol catalyzed by Y-type zeolite, in which the Na^+ had been replaced by copper(II) ion, has been investigated in a flow system with reaction temperature between 300 to 390°C. The main oxidation products were benzaldehyde, CO_2, and CO. The main active site for this oxidation was found to be Cu(II) ion in the zeolite. The rate for benzaldehyde formation was best described as first order in oxygen and reciprocal first order in benzyl alcohol, respectively ($r_{\phi CHO} = k \cdot [O_2]^1[\phi CH_2OH]^{-1}$), and an apparent activation energy of 13.6 kcal/mol was observed on this basis in the temperature range 330 to 390°C. The catalytic activity for the oxidation of benzyl alcohol was found to be affected by the addition of amine. Piperidine addition increased the oxidation activity, while pyridine addition decreased the oxidation activity. The bonding parameters obtained from ESR measurement of Cu(II)NaY–amine systems indicate that covalent bonding strength between Cu(II) and piperidine is stronger than that with pyridine. A reaction mechanism for the oxidation of benzyl alcohol to benzaldehyde over Cu(II)NaY was proposed on the basis of the results obtained.

INTRODUCTION

Metal ion-exchanged Y-type zeolites have been the subject of many publications, particularly from the point of view of structure, adsorption properties, and catalytic activities (*1*). Among the transition metal ions, it has been shown that the Cu(II) ion is an ideally suited component for the electron spin resonance (ESR) study of crystalline environments in the supercage of Y-type zeolite (*2*). Some oxidation reactions of hydrocarbons over such zeolites have been attempted. Mochida and his co-workers (*3*) have reported the oxidation reaction of cyclohexane and propylene over a Cu(II)NaY zeolite catalyst. However, the oxidation of hydrocarbons and/or nonhydrocarbons over the transition metal ion-exchanged zeolites has not been attempted much so far. The transition metal ions exchanged on the zeolite are considered to exhibit to a certain extent chemical natures similar to those in the homogeneous system (*1*b). It is interesting to compare the catalytic behavior of transition ion-exchanged zeolite with that of a homogeneous transition metal complex.

It is the purpose of this study to investigate systematically the reactivity of the copper(II) ion-exchanged Y-type zeolite [Cu(II)NaY] in the vapor-phase oxidation of benzyl alcohol. From the kinetic results on benzyl alcohol oxidation over Cu(II)NaY catalyst, it was found that the formation rate of benzaldehyde showed a first-order dependence on the partial pressure of oxygen and an inverse first-order dependence on the partial pressure of benzyl

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alcohol. The effects of some amine addition to the Cu(II)NaY catalyst on the oxidation activity was also investigated. The addition of some amine to the reaction system was found to have a specific effect on the oxidation activity. From ESR spectra of a Cu(II)NaY catalyst with adsorbed amine, the bonding parameters between Cu(II) ion and amine were estimated. These ESR results and the estimated bonding parameters were discussed in connection with the oxidation activity of Cu(II)NaY catalysts.

EXPERIMENTAL

Materials. Cu(II)NaY samples with various Cu(II) ion contents were prepared, starting from SK-40(NaY) supplied by Linde Division, Union Carbide. Analysis of the starting zeolite (SK-40) on an anhydrous basis is as follows: SiO_2, 63.5 wt%; Al_2O_3, 23.5 wt%; Na_2O, 13.0 wt%. SK-40 was impregnated in aqueous sodium acetate (1 mol/liter) for 1 week and dried at 120°C for 2 days. The material was then treated by conventional ion-exchange methods with a $CuCl_2$ solution (10 wt%), the concentration of which was calculated to obtain the required exchange level. The high exchanged samples were obtained by treating the zeolite several times with the metal ion solution (*10*). The solids were then washed in distilled water to remove the excess salts and dried at 120°C in an oven. The degree of ion exchange was determined by analyzing the resulting solutions for copper(II) by colorimetry. An H–Y zeolite was prepared by exchanging with an ammonium chloride solution and subsequently heating of the exchanged zeolite. The degrees of ion exchange was determined by atomic absorption analysis of the residual sodium ions. Mean surface areas of these catalysts, measured by the BET method with N_2, were 442 to 600 m^2/g. The increase of copper(II) exchange level gradually caused the decrease of surface area. Preheating treatments of these catalysts had no influence on surface areas. In the X-ray diffraction measurement of these catalysts, a Rigaku Denki diffractometer (Model Geigerflex D-3F) was used employing filtered Cu$K\alpha$ radiation at 35 kV and 15 mA. The sample was scanned over a 2θ range of 60° to 2° using $CaCO_3$ ($2\theta = 29.38$) as an internal standard. The catalyst was shown to be highly crystalline. The exchanged zeolites were pelleted under a 300-kg/cm^2 pressure for 1 hr without a binder and crushed and sized to 20 to 32 mesh. Benzyl alcohol (G.R. grade) was obtained from Nakarai Chemicals Co. and was used without further purification. Pyridine and piperidine were obtained from Nakarai Chemicals Co. and were purified by distillation. Oxygen, nitrogen, carbon monoxide, and hydrogen were purchased commercially and were passed through silica gel before use.

Apparatus and procedure. Reactions were carried out at 1 atm in a fixed bed flow reactor. The catalyst bed was diluted with silica sand to increase its heat capacity. The reactor was a 15-mm-i.d. silica tubing placed in a vertical furnace. The thermowell was located in the middle of catalyst bed packed in a reactor. Prior to the reaction, the catalyst was heated in a gas flow of the reaction condition at various temperatures for 2 hr. The flow rates of oxygen and nitrogen were measured by means of a capillary flowmeter. Benzyl alcohol was pumped into the preheating zone of the reactor using a microfeeder. The liquid product and unreacted benzyl alcohol were collected in a methanol trap maintained at −10 to −20°C and analyzed by a gas chromatograph (Shimazu GC-3AH) with a thermal conductivity detector using a 3-m stainless-steel column (diameter, 3 mm) packed with 10% silicone OV-17 on Chromosorb GAW DMCS operating at 195°C with hydrogen as a carrier gas (50 ml/min). Gaseous products were collected in a 1-ml gas sampler tube connected with the reactor. The gaseous products were analyzed by means of gas chromatography (Yanagimoto G 800-T) with the intermediate cell method (*4*) using two 40-cm columns packed with silica gel (60–80 mesh) and a 2-m column packed with 5A molecular sieves (40–60 mesh) operating at 85°C with hydrogen as a carrier gas (50 ml/min). The main oxidation products were benzaldehyde, carbon dioxide, and carbon monoxide. Depending upon the reaction conditions, toluene, benzoic acid, and benzyl ether were obtained as minor products. The conversion of benzyl alcohol, the yield of benzaldehyde, and the selectivity of benzaldehyde were defined as follows:

$$\text{Conversion } (\%) = \frac{\text{moles of benzyl alcohol reacted}}{\text{moles of benzyl alcohol fed}} \times 100.$$

$$\text{Yield } (\%) = \frac{\text{moles of benzaldehyde produced}}{\text{moles of benzyl alcohol fed}} \times 100.$$

$$\text{Selectivity } (\%) = \frac{\text{moles of benzaldehyde produced}}{\text{moles of benzyl alcohol reacted}} \times 100.$$

As a measure of contact time, W/F is defined as

$$W/F = \frac{\text{catalyst weight (grams)}}{\text{feed rate of reactants (benzyl alcohol + oxygen + nitrogen) (mole per hour)}}$$

Kinetic treatment. For the kinetic experiments, the dependence of the reaction rate on partial pressure of benzyl alcohol was examined using Cu(II)NaY-19[1] as a catalyst at 340°C by keeping the partial pressure of oxygen constant. The partial pressure of nitrogen was varied to keep W/F constant at 0.36 $\text{g/mol}\cdot\text{hr}^{-1}$. The dependence of the rate on the partial pressure of oxygen was examined in the same manner. The partial pressure of benzyl alcohol and W/F were kept constant.

Electron spin resonance (ESR) measurements. The ESR studies were made with a JEOL spectrometer (Model 3BS-X). The instrument was operated at X-band with a 100 kHz modulation unit. The g values were determined by using a 2,2′-diphenyl-1-picrylhydrazyl ($g = 2.0036$) standard attached to the outside of the sample tube. All of the ESR measurements were carried out either at room temperature or at liquid nitrogen temperature.

Infrared measurements. All infrared measurements were made with the catalysts in the form of wafers prepared by compressing 20 to 40 mg of fine powder into ca. 20-mm-diameter disk at 300 kg/cm^2 for 1 hr. The wafers were electrically heated at various temperatures and atmospheres after calcination and evacuation in an infrared *in situ* cell (NaCl windows) attached to a conventional vacuum system. The spectra of the wafers were recorded at room temperature. Infrared spectra were recorded using a Hitachi 215 spectrophotometer and a Nippon Bunko DS-402G spectrophotometer.

RESULTS

Oxidation of Benzyl Alcohol

The main oxidation products from the gas-phase oxidation of benzyl alcohol over Cu(II)NaY zeolite were benzaldehyde,

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[1] Cu(II)NaY-19 refers to a Y-type zeolite in which 19% of the Na^+ ions have been exchanged by Cu(II) ions.

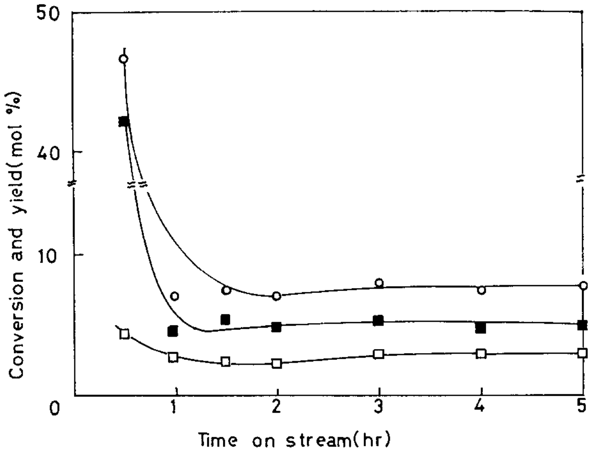

FIG. 1. Activity of Cu(II)NaY on benzyl alcohol oxidation. Catalyst, Cu(II)NaY-67; W/F, 0.36 g/mol·hr^{-1}; reaction temperature, 340°C; P_b, 0.026 atm; P_{O_2}, 0.184 atm; ○, conversion of benzyl alcohol; □, yield of benzaldehyde; ■, yield of CO_2 and CO.

carbon dioxide, and carbon monoxide. As an example, the variation in the catalytic activity with time is illustrated (Fig. 1) in the case of Cu(II)NaY-67 under the following reaction conditions: reaction temperature, 340°C; W/F, 0.36 g/mol·hr^{-1}; partial pressure of benzyl alcohol, 0.026 atm; and partial pressure of oxygen, 0.184 atm. The catalytic activity markedly decreased at the reaction time of 30 min, and it decreased to 9% at the reaction time of 1.5 hr. However, we did not study what happened to the catalyst before reaching steady state. It is evident that steady-state activity is obtained after a reaction time of 1.5 to 2 hr, and the selectivity of the reaction product does not vary with time on stream. In Table 1, the activity, the yield, and the selectivity for the production of benzaldehyde on various forms of zeolites are compared. The listed values refer to the data after the reaction has run 2 to 3 hr. From Table 1, it was found that Cu(II)NaY catalyst had higher activity for this oxidation reaction than NaY. On the other hand, HY was found to have high selectivity for the production of benzaldehyde, though its activity is rather low. Thus it was supposed that Cu(II)NaY catalyst has both activities for deep and partial oxidation under the present reaction conditions. In Table 1, Cu(I)NaY refers to the Cu(II)NaY zeolite treated with carbon monoxide at 400°C for 2 hr before reaction. These Cu(I)NaY catalysts have lower activity than the original Cu(II)NaY catalysts. The partial reduction of Cu(II) ion in zeolite by the pretreatment of Cu(II)NaY with carbon monoxide before oxidation reaction may be considered to cause the low oxidation activity for benzyl alcohol.

Effect of the Cu(II) Ion Exchanged

The effect of the Cu(II) ion exchanged on the conversion and the yield of benzalde-

TABLE 1

Benzyl Alcohol Oxidation over Some Zeolites[a]

Catalyst	Conversion of benzyl alcohol (mol%)	Yield of benzaldehyde (mol%)	Selectivity of benzaldehyde (%)
Cu(II)NaY-37	3.3	1.5	46
Cu(II)NaY-45	4.7	1.6	34
Cu(II)NaY-67	8.0	3.0	38
Cu(I)NaY-37[b]	1.7	0.8	47
Cu(I)NaY-45	2.4	0.9	37
HY	1.0	1.0	100
NaY	1.5	0.6	40

[a] Temperature, 340°C; W/F, 0.36 g of cat/mol·hr^{-1}; catalyst, 0.523 g; $P_{\phi CH_2OH}$ = 0.026 atm; P_{O_2} = 0.184 atm; calcination, 350°C, 2 hr.

[b] 400°C, 2 hr of CO treatment before reaction.

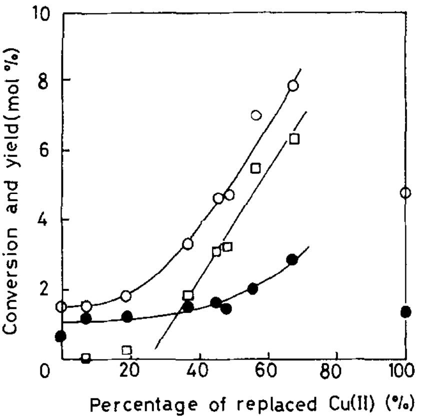

FIG. 2. Effect of percentage of exchanged Cu(II) ion. W/F, 0.36 g/mol·hr^{-1}; calcination temperature, 350°C; reaction temperature, 340°C; P_b, 0.026 atm; P_{O_2}, 0.184 atm; ○, conversion of benzyl alcohol; ●, yield of benzaldehyde; □, conversion of benzyl alcohol due to Cu(II) ion (see text).

hyde are shown as a function of the percentages of ion exchange in Fig. 2, where the conversion and the yield are the steady-state values at the reaction time of 2 to 3 hr. The conversion increased with an increasing percentage of Cu(II) ion and did so rather abruptly beyond about 30% Cu(II) ion exchange, whereas only a small variation is observed in that of activity in the cases of below 30% exchange. However, the activity of 100% exchanged Cu(II)NaY catalyst decreased rather sharply as shown in Fig. 2.

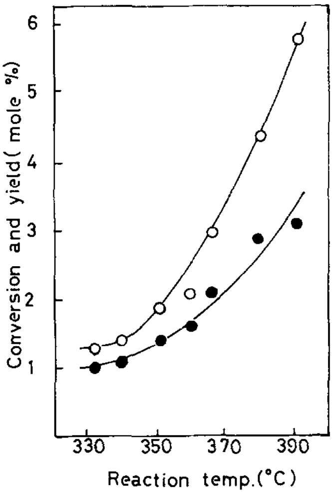

FIG. 3. Variation of the conversion of benzyl alcohol and the yield of benzaldehyde with reaction temperature. Catalyst, Cu(II)NaY-19; calcination temperature, 400°C; W/F, 0.36 g/mol·hr^{-1}, P_b, 0.026 atm; P_{O_2}, 0.184 atm; ○, conversion of benzyl alcohol; ●, yield of benzaldehyde.

Effect of the Reaction Temperature

With a constant contact time and molar ratio of the reactants, the effect of the reaction temperature on the conversion and the yield were examined with Cu(II)NaY-19 as a catalyst. As shown in Fig. 3, the conversion of benzyl alcohol and the yield of benzaldehyde monotonously increased with the reaction temperature. The selectivity to benzaldehyde is approximately constant below 350°C but falls sharply at higher temperatures.

Effect of the Pretreatment Temperature and H_2O Addition

The effect of the pretreatment temperature in the range of 310 to 500°C on the conversion and the yield was studied with Cu(II)NaY-56 at a reaction temperature of 300°C. Figure 4 shows the variations in the conversion of benzyl alcohol and the yield of benzaldehyde at various pretreatment temperatures. At first the conversion and the yield increase with pretreatment temperature and then go through maxima at 350°C and decrease at higher temperatures. Thus the reasonable pretreatment

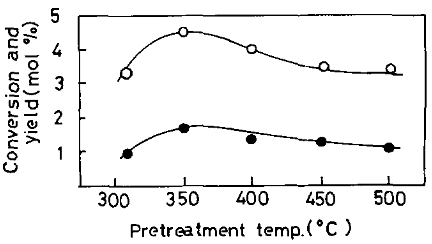

FIG. 4. Effect of pretreatment temperature on the conversion and the yield. Catalyst, Cu(II)NaY-56; W/F, 0.67 g/mol·hr^{-1}; P_b, 0.05 atm; P_{O_2}, 0.2 atm; reaction temperature, 300°C; ○, conversion of benzyl alcohol; ●, yield of benzaldhyde.

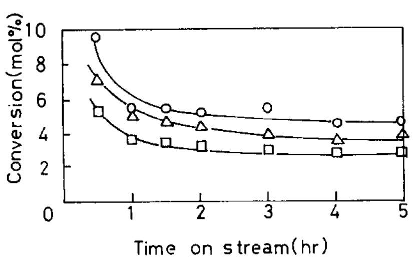

FIG. 5. Effect of addition of water on the conversion of benzyl alcohol. Catalyst, Cu(II)NaY-48; calcination temperature, 350°C; W/F, 0.36 g/mol $\cdot$hr^{-1}; P_b, 0.026 atm; P_{O_2}, 0.184 atm; reaction temperature, 340°C; ○, no water; △, addition of water (0.01 mole ratio) to benzyl alcohol; □, addition of water (0.05 mole ratio) to benzyl alcohol.

temperature is around 350°C. Figure 5 shows the variation of the conversion of benzyl alcohol with time when various amounts of H_2O are added: the more H_2O added, the lower the oxidation activity. This evidently indicates that H_2O addition causes deactivation in the oxidation of benzyl alcohol, but since the activity becomes inversely lower at preheating temperatures higher than 350°C as described above, it is considered that a small amount of water within a zeolite cage, which may be eliminated at higher pretreatment temperatures, is necessary for the present oxidation activity.

Pretreatment Effect with CO and H_2

The effect of pretreatments with CO and H_2 on the conversion of benzyl alcohol and the selectivity for benzaldehyde was examined under the following reaction conditions: $W/F = 0.36$ g/mol$\cdot$hr^{-1}; reaction temperature, 340°C. Figure 6 shows the variations in the conversion and the selectivity with percentage of replaced Cu(II) ion in pretreatments with CO and H_2, in addition to the case of only calcination at 350°C. The conversions of benzyl alcohol in both cases of pretreatment of Cu(II)NaY with CO and H_2 became lower than that on a Cu(II)NaY catalyst only calcinated at 350°C, independent of the degree of Cu(II) ion exchange. The difference in the behaviors of CuNaY catalysts with CO and H_2 is the selectivity for benzaldehyde. Thus Cu(II)NaY pretreated with H_2 has the higher selectivity than the one pretreated with CO. From ESR and ir spectroscopy, Naccache and Taarit (*5*) have reported that Cu(II) ions in Cu(II)-NaY were reduced to Cu(I) ions by CO treatment, and hydrogen reduction resulted in the formation of metallic copper. This difference in the reduction state of Cu(II) ions may be considered to affect the selectivity for benzaldehyde.

Kinetic Treatment

Reaction kinetics were examined on Cu(II)NaY-19, which had a high selectivity for benzaldehyde at 340°C. Since the yield of benzaldehyde was below 5 mol%, the principle of the differential reactor could be applied. The reaction rate (r) of differential reactor for benzaldehyde formation may be generally expressed by Eq. (1), where k, P_{O_2}, and P_b are the rate constant and partial pressures of oxygen and benzyl alcohol, respectively; m and n are the

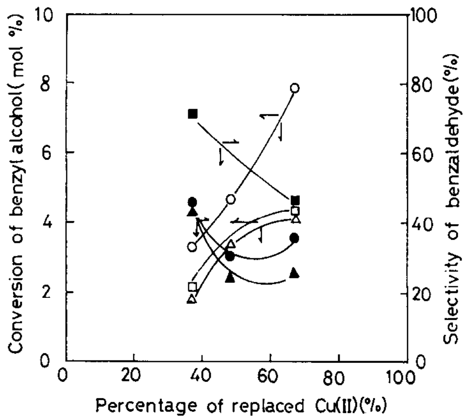

FIG. 6. Effect of pretreatments with CO and H_2 on the conversion of benzyl alcohol and the selectivity for benzaldehyde. W/F, 0.36 g/mol$\cdot$hr^{-1}; pretreatment temperature, 400°C; reaction temperature, 340°C; P_b, 0.026 atm; P_{O_2}, 0.184 atm; ○ and ●, calcination at 350°C; △ and ▲, pretreatment with CO; □ and ■, pretreatment with H_2.

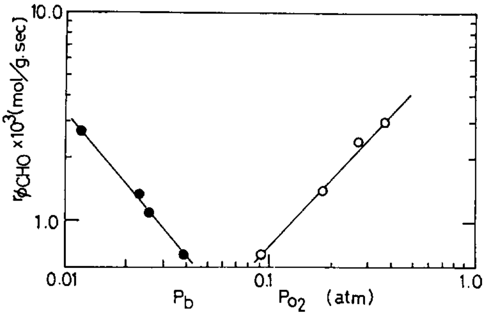

FIG. 7. Log–log plots of the formation rates of benzaldehyde vs the partial pressures of benzyl alcohol and oxygen. Catalyst, Cu(II)NaY-19; calcination temperature, 350°C; W/F, 0.36 g/mol $\cdot hr^{-1}$; reaction temperature, 340°C; ○, plots as for O_2; ●, plots as for benzyl alcohol.

reaction orders in oxygen and benzyl alcohol, respectively. Relations between $\log r$ vs $\log P_D$ are shown in Fig. 7.

$$r = x/(W/F) = k\cdot P_{O_2}{}^{m}\cdot P_b{}^{n} \qquad (1)$$

The values of m and n are calculated for benzaldehyde formation from Fig. 7.

$$r = k\cdot P_{O_2}{}^{1}\cdot P_b{}^{-1} \qquad (2)$$

The rate equation thus obtained is described by Eq. (2) for benzaldehyde formation.

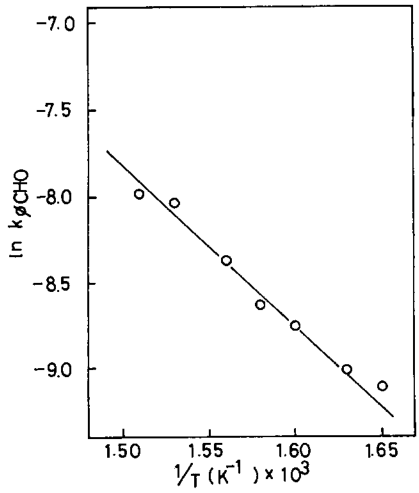

FIG. 8. Arrhenius plots for oxidation of benzyl alcohol to benzaldehyde. Catalyst, Cu(II)NaY-19; calcination temperature, 400°C; W/F, 0.36 g/mol $\cdot hr^{-1}$; P_b, 0.026 atm; P_{O_2}, 0.184 atm.

An Arrhenius plot for the formation rate of benzaldehyde in the temperature range of 330 to 390°C was prepared, as shown in Fig. 8, in order to obtain the apparent activation energy for benzaldehyde formation, which was calculated to be 13.6 kcal/mol from the slope of the straight line in Fig. 8.

Effect of the Addition of Some Amine on the Oxidation of Benzyl Alcohol over a Cu(II)NaY Catalyst

The effect of amine addition on the conversion of benzyl alcohol and the yield of benzaldehyde was examined using pyridine and piperidine at a reaction temperature of 340°C over a Cu(II)NaY-45 catalyst and one (Cu(II)NaY-45) pretreated with CO at 400°C for 2 hr. The addition of pyridine showed a trend toward decreasing conversion of benzyl alcohol and decreasing yield of benzaldehyde. Furthermore, the conversion of benzyl alcohol and the yield of benzaldehyde over copper-ion-exchanged zeolite pretreated with CO decreased more than those for reactions over Cu(II)NaY, independent of the amount of pyridine addition. Figure 10 indicates the variation of the conversion of benzyl alcohol and the yield of benzaldehyde with mole ratio of piperidine to benzyl alcohol over a Cu(II)-NaY-45 catalyst and the same catalyst pretreated with CO at 400°C for 2 hr. In

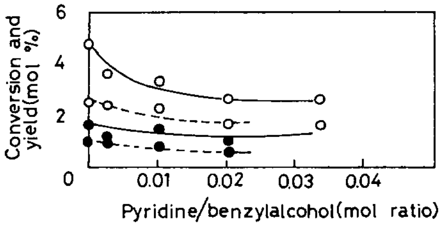

FIG. 9. Effect of addition of pyridine on the conversion of benzyl alcohol and the yield of benzaldehyde. W/F, 0.36 g/mol$\cdot hr^{-1}$; P_b, 0.026 atm; P_{O_2}, 0.184 atm; reaction temperature, 340°C; ○, conversion of benzyl alcohol; ●, yield of benzaldehyde; ——, Cu(II)NaY-45; – – –, Cu(I)NaY-45 (Cu(II)NaY-45 pretreated with CO before reaction).

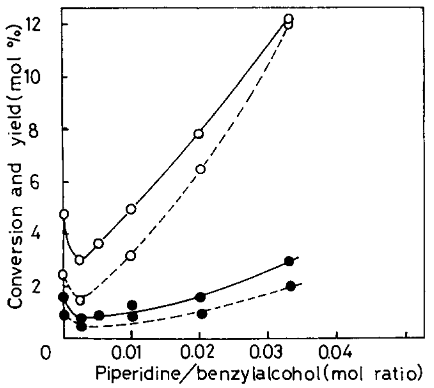

FIG. 10. Effect of addition of piperidine on the conversion of benzyl alcohol and the yield of benzaldehyde. W/F, 0.36 g/mol·hr^{-1}; P_b, 0.026 atm; P_{O_2}, 0.184 atm; reaction temperature 340°C; ○, conversion of benzyl alcohol; ●, yield of benzaldehyde; ———, Cu(II)NaY-45; – – –, Cu(I)NaY-45 (Cu(II)NaY-45 pretreated with CO before reaction).

the initial stage of the addition of piperidine, both the conversion of benzyl alcohol and the yield of benzaldehyde tended to decrease up to a mole ratio of piperidine to benzyl alcohol of 0.0025 and to increase at mole ratios higher than 0.0025 as shown in Fig. 10. Although the conversion and the yield over Cu(I)NaY catalyst are lower than those over Cu(II)NaY catalyst, the catalytic behaviors in both catalytic systems with piperidine addition show similar trends. These results just described suggest that piperidine acts as a poison and an accelerator for the present oxidation over copper ion-exchanged Y-type zeolite catalyst; on the other hand, pyridine which is weaker base than piperidine, functions only as a poisonous additive under the present reaction conditions. We have tried to measure the ESR and ir spectra of these Cu(II)NaY catalysts adsorbed with either pyridine or piperidine to investigate the role of these amines.

ESR Spectra of Copper(II) Ion-Exchanged Y-Type Zeolite

Figure 11 indicates the ESR spectra at 77°K of Cu(II)NaY-7 zeolites evacuated at 350°C for 2 hr and pretreated with CO at 400°C for 2 hr. As evidenced from Fig. 11, it was found that the ESR anisotropic spectra consisted of four absorption peaks and one large peak, which were attributed to the copper(II) ion ($I = \frac{3}{2}$) surrounded by a typical axis symmetrical environment, in the low and high magnetic fields, respectively (*6*). The absorption intensity of ESR spectrum b that was pretreated with CO is appreciably weak in comparison with the one of a that was only evacuated at 350°C. Thus it is considered that significant amounts of Cu(II) ion in Y-type zeolite are reduced to Cu(I) ion by the method of pretreatment with CO (*7*). The intensity of ESR spectrum c in Fig. 11 pretreated with CO after diethylamine was adsorbed in Cu(II)NaY-7 at room temperature was found to decrease remarkably. This amine effect may result from the charge transfer from amine coordinated to Cu(II) ion (*8*). Figure 12 demonstrates the ESR spectra of Cu(II)

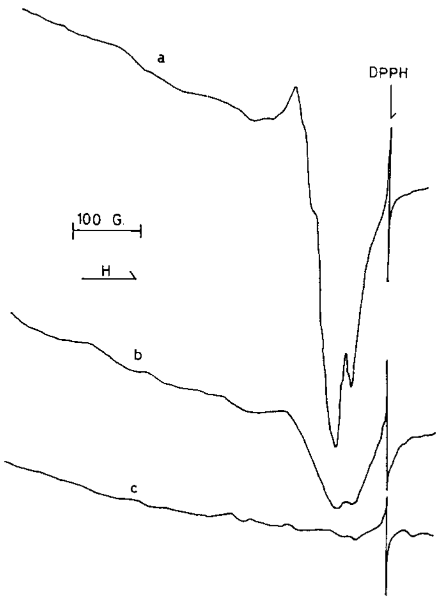

FIG. 11. ESR spectra of Cu(II)NaY-7 at 77°K. a, after evacuation at 350°C for 2 hr; b, after CO treatment at 400°C for 2 hr; c, diethylamine was adsorbed at room temperature before treatment as in b.

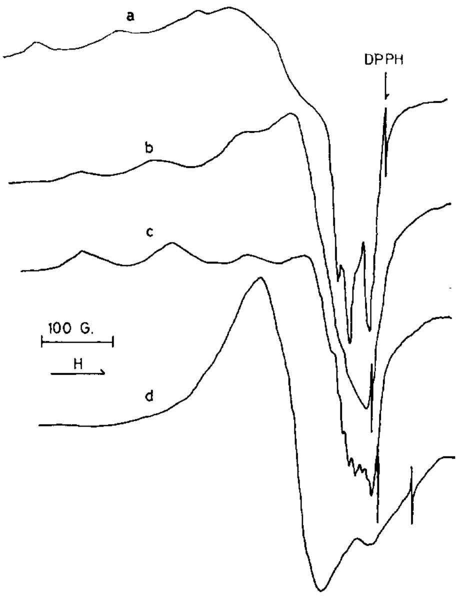

FIG. 12. ESR spectra of Cu(II)NaY-37 adsorbed with some amines. a, after evacuation at 350°C for 2 hr; b, pyridine was adsorbed at 150°C (20 Torr); c, piperidine was adsorbed at 150°C (20 Torr); d, diethylamine was adsorbed at 20°C (20 Torr).

NaY-37 adsorbed with some amines. It is evident that in the case of piperidine adsorption, about seven ESR adsorption peaks with coupling constant 15 *G* were observed in superposition to one large peak in the high magnetic field region based on Cu(II) ion. These newly generated peaks are considered to be a superhyperfine structure resulting to a certain extent from the transfer of an odd electron in the Cu(II) ion to a nitrogen atom ($I = 1$) of piperidine (*8*). In contrast to ESR spectrum c just described, the ESR spectrum of Cu(II)NaY-37 adsorbed with pyridine had no superhyperfine structure at the present measurement condition as shown in Fig. 12b. Thus this result is considered to show that piperidine interacts covalently more strongly with Cu(II) ions in Y-type zeolites than pyridine does. Furthermore, it was found that the value of the parallel coupling constant ($A_{\parallel}$) for piperidine adsorption (189.8 *G*) was larger than that for pyridine adsorption (167.0 *G*), a result supporting the suggestion about the strengths of covalent interaction of the two amines with Cu(II) ions described above. ESR spectrum d in Fig. 11 adsorbed with diethylamine, in contrast to ESR spectra b and c, consists of a rather symmetrical broad absorption peak, an observation which may indicate that Cu(II) pairs are formed in the zeolite cavity as discussed by Lunsford and his co-worker (*9*).

Infrared Spectra of Copper(II) Ion-Exchanged Y-Type Zeolites

The ir spectra of piperidine adsorbed Cu(II)NaY-19 under various measurement conditions are shown in Fig. 13. All samples were first evacuated at 300°C for 2 hr. After adsorption of piperidine at room temperature, they were once more heated at a series of temperatures under a residual pressure of about 10^{-3} Torr, the disks were then cooled to room temperature, and ir spectra were recorded. When piperidine was added to the precalcinated sample at 300°C, a broad absorption band appeared in the region of less than 1440 cm^{-1} (Fig. 13b). Evacuation at room temperature to remove any piperidine possibly present on the sample caused the appearance of the

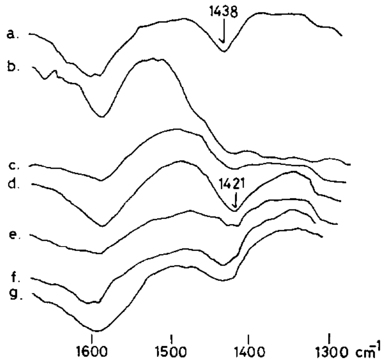

FIG. 13. The ir spectra of piperidine adsorbed in Cu(II)NaY-19. a, Cu(II)NaY-19 evacuated at 300°C for 2 hr; b, piperidine was adsorbed at room temperature (37 Torr); c, evacuated at room temperature for 30 min; d, evacuated at 100°C for 10 min; e, evacuated at 150°C for 20 min; f, evacuated at 250°C for 30 min; g, evacuated at 350°C for 2 hr.

1421-cm^{-1} peak (Fig. 13c). Similarly upon evacuation of the sample at 100°C for 10 min, the 1421-cm^{-1} peak became more sharp as shown in 13d. Further increases of evacuation temperature resulted in decrease of the intensity of the 1421-cm^{-1} peak (Figs. 13e and f, but as evidenced in Fig. 13g this peak remained as a shoulder, even at evacuation temperatures as high as 350°C). The peak at 1421 cm^{-1} is considered to be the one which N–H deformation frequency at 1440 cm^{-1} shifted to the lower frequency region. Thus piperidine is considered to be coordinatively absorbed on copper(II) ion and give rise to an ir band at 1421 cm^{-1}. We may also conclude that the Cu(II)-piperidine complex formed in the zeolite is moderately stable from the ir spectra.

DISCUSSION

Oxidative Property of Copper Ion-Exchanged Y-Type Zeolite

As described above, the copper(II) ions in Y-type zeolite appear to be directly involved in the partial and deep (perfect) oxidation process of benzyl alcohol. In particular, the deep oxidation was predominant at reaction temperatures of more than 370°C. The conversion of benzyl alcohol and the yield of benzaldehyde as a function of replaced Cu(II) ion are plotted in Fig. 2 for a reaction temperature of 340°C. For the lower exchange levels of Cu(II) ions, the oxidation activity (conversion and yield) did not increase as much with an increase in exchanged Cu(II) ions, but the conversion of benzyl alcohol increased almost linearly with an increase in exchanged Cu(II) ions for the higher exchange levels. It was also found that the higher Cu(II)-exchanged catalyst was more effective for deep oxidation than the partial one. The considerable drop in the oxidation activity for the 100% exchanged catalyst may be partly due to less proton-acid sites on the exhaustively exchanged Cu(II)NaY than the partially exchanged Cu(II)NaY, as suggested by Ward (*10*). The catalytic activities due to copper(II) ions were calculated by subtracting the activity of NaY from those of Cu(II)NaY, and the plots (□) are shown in Fig. 2. The activity due to Cu(II) ions appeared virtually beyond 25% Cu(II) ion-exchange and increased linearly with an increase in exchanged Cu(II) ions. This straight line intersected with the abscissa at 25% ion exchange. Mochida and his co-workers (*11*) have recently studied the catalytic oxidative dehydrogenation of cyclohexane over copper(II) ion-exchanged Y-type zeolite, and investigated the relation between the formation rate and percentage of the copper(II) ion exchange to suggest that the catalytically active sites on the zeolite were copper(II) ions exchanged to the exchangeable sites beyond 20% preferential exchange of site I, consistent with the facts obtained in the present study. Accepting the nomenclature for cation sites within the zeolite structure suggested by Smith *et al.* (*12*), it is probable that only Cu(II) ions located at Site II within the zeolite supercage are accessible to the reactant and therefore contribute to catalysis, and Cu(II) ions within the sodalite units at Sites I′ and II′, or within the hexagonal prisms at Site I, are then inaccessible as suggested by Rudham and Sanders (*13*).

It was found that the conversion of benzyl alcohol and the yield of benzaldehyde increased with pretreatment temperatures up to 350°C, but fell at higher temperatures. This behavior of the oxidation activity may indicate that water molecules adsorbed near copper(II) ions in the cavity are easily ionized because of the strong electrostatic field in the cavity of Cu(II)-NaY, as has been postulated by the other workers (*10, 14*), and Bronsted acidity results, which is considered to be effective to some extent for the present oxidation reaction, in addition to the action of Cu(II) ions themselves. The low oxidation activity of Cu(II)Y-100 may be interpreted as resulting from less Bronsted acids on exhaustively Cu(II) ion-exchanged zeolites than on partially exchanged ones, as described above. Gentry *et al.* (*15*) have reported that propylene oxidation on X-type zeolite containing Cu(II) ions depended upon both the acidity of the zeolite and the nature of the Cu(II) ions; on the other hand, the acidic properties of the catalyst were unimportant in methane oxidation. However, as shown in Fig. 5, too much water acts inversely as a poison. This fact may indicate that excess water is attracted to the Cu(II) ion to form a hydrated Cu(II) ion, a form exhibiting lower activity for the present oxidation.

Catalytic Activity of Copper(II)-Amine Y-Type Zeolite System

It is well known that a variety of homogeneous copper(II)-amine complexes act as catalysts for oxidation reactions of a number of organic substrates (*16*). Vansant and Lunsford (*7*) have studied the ESR spectra of some copper(II)-ammonia, -monomethylamine, and -monoethylamine complexes in ion-exchanged Y-type zeolites under various adsorption and desorption conditions. As shown in Figs. 9 and 10, piperidine addition caused an increased conversion of benzyl alcohol; on the other hand, pyridine addition decreased the conversion of benzyl alcohol. As one of the measures of interaction between copper(II) ion and piperidine or pyridine in zeolite, the bonding parameters of these copper(II) complexes were calculated by the method of Maki and McGarvey (*17*) and Kivelson and Neiman (*18*) using the magnetic parameters obtained by ESR measurement of these copper(II) complexes. The results are shown in Table 2. The notations of Maki and McGarvey for a square-planar complex will be used here. The value of the α^2 parameter is a measure of the σ bonding strength between the $d_{x^2-y^2}$ copper orbital and the σ orbitals of the four ligands in the xy plane, and the β_1^2 parameter value is a measure of the in-plane π bonding of the d_{xy} copper orbital. The values of the bonding parameters were calculated in the same manner as reported previously (*19*). $\Delta E_{xy}(= E_{xy} - E_{x^2-y^2})$, the ligand field energy, was estimated as 10,500 cm^{-1}. From the values of α^2 and β_1^2 calculated, it is evident that both piperidine and pyridine coordinate with copper(II) ions in the zeolite. Furthermore by the comparison of the values of these calculated bonding parameters between piperidine and pyridine system, differences of bonding nature of copper(II) ion between piperidine and pyridine may be shown. The α^2 of the copper(II)-piperidine system is smaller than that of the copper(II)-pyridine system. This result seems to indicate that the covalent σ bond between copper(II) ion and the nitrogen atom of piperidine is stronger than the one between copper(II) ion and the nitrogen atom of pyridine. Also the β_1^2 value, a measure of the in-plane π bonding, of the copper(II)-piperidine system was less than that of the copper(II)-pyridine system. These results seem to indicate that the covalent bond between copper(II) ion and piperidine is stronger than the one between copper(II) ion and pyridine. It may be concluded that the copper(II) ion with a more strongly covalently bonded amine has a higher oxidation activity for benzyl alcohol, consistent with the result that with piperidine addition to the Cu(II)NaY zeolite catalyst, the oxidation activity was higher than with pyridine addition. Vansant and Lunsford (*8*) have reported all α^2 values were around 0.75 for

TABLE 2

Bonding Parameters of Copper(II) Complexes in Y-Type Zeolites

Complex	$g_{\parallel}$	$g_{\perp}$	α^2	β_1^2
Cu(II)-piperidine	2.374	2.074	0.70	0.53
Cu(II)-pyridine	2.234	2.072	0.89	0.66

the different ammoniated copper(II)NaY zeolite. It is interesting to note that α^2 values of ammoniated copper(II)NaY zeolites are between α^2 values of copper(II)–piperidine and copper(II)–pyridine systems.

Reaction Mechanism of Benzaldehyde Formation on Cu(II)NaY

To satisfy the observed rate [Eq. (2)] of benzaldehyde formation, we propose the following mechanism as one of the possible reaction series for benzaldehyde formation on a Cu(II)NaY zeolite catalyst: $\mathrm{Cu}(v) = \mathrm{Cu}(T) - \mathrm{Cu{-}O_2} + \mathrm{Cu{-}C_6H_5CH_2OH} + \mathrm{Cu{-}C_6H_5CHO}$, where $\mathrm{Cu}(v)$ is the Cu(II) ion without adsorbed molecules, and $\mathrm{Cu}(T)$ is the total copper(II) ion in the zeolite catalyst. Molecular adsorption of oxygen and adsorption of benzyl alcohol on the active Cu(II) ions of the catalyst are considered as a first step [Eqs. (3) and (4)]. Equation (5) which is considered as the rate-determining step shows the surface reaction of two adsorbed species on the separate active sites of the zeolite catalyst. Equation (6) describes the desorption process of benzaldehyde formed.

$$\mathrm{Cu}(v) + \mathrm{O_2} \overset{K_1}{\rightleftharpoons} \mathrm{Cu{-}O_2} \tag{3}$$

$$\mathrm{Cu}(v) + \mathrm{C_6H_5CH_2OH} \overset{K_2}{\rightleftharpoons} \mathrm{Cu{-}C_6H_5CH_2OH} \tag{4}$$

$$\mathrm{Cu{-}O_2} + \mathrm{Cu{-}C_6H_5CH_2OH} \xrightarrow{k} \mathrm{Cu{-}C_6H_5CHO} + \mathrm{Cu}(v) \tag{5}$$

$$\mathrm{Cu{-}C_6H_5CHO} \overset{K_3}{\rightleftharpoons} \mathrm{C_6H_5CHO} + \mathrm{Cu}(v) \tag{6}$$

If it is assumed that K_2 and $K_3 \gg K_1$, the formation rate of benzaldehyde, $r_{\phi\mathrm{CHO}}$ is expressed as follows:

$$r_{\phi\mathrm{CHO}} = \frac{k \cdot K_1}{K_2} \cdot \frac{[\mathrm{Cu}(T)] \cdot [\mathrm{O_2}]}{[\mathrm{C_6H_5CH_2OH}]} \tag{7}$$

$$= k' \cdot \frac{[\mathrm{O_2}]}{[\mathrm{C_6H_5CH_2OH}]} \tag{8}$$

where

$$k' = \frac{k \cdot K_1}{K_2} \cdot [\mathrm{Cu}(T)]. \tag{9}$$

Recently Huang (*20*) has conducted the adsorption study of CO, ammonia, and other gases over Cu(II)NaY zeolite and reported the results of the infrared study of cuprous carbonyl complexes in Y-type zeolite, with or without the presence of other ligands such as ammonia, ethylenediamine, or pyridine. Also Huang and Vansant (*21*) have reported adsorption of ammonia on a Cu(II)NaY sample would pull most copper(II) ions out of the small cavities to form copper(II)–ammonia complexes. In his recent review (*1*b), Lunsford has demonstrated that it is possible to synthesize and characterize transition metal complexes within the zeolite cavities, and several of the complexes exhibit catalytic activity. In the case of present study, added piperidine may be considered to pull copper(II) ions out of small cavities more strongly than pyridine molecules do and thus form copper(II) complexes in the supercage which have catalytic activity for benzyl alcohol oxidation.

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