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Oxidation of Benzyl Alcohol over Co(II)NaY Zeolites

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Benzyl alcohol oxidation was carried out with a Y-type zeolite catalyst ion-exchanged with cobalt(II) ion (Co(II)NaY) in a flow system operated at atmospheric pressure and temperatures of 320 to 390°C. The Co(II)NaY catalyst was found to have high selectivity for benzaldehyde, a partial oxidation product, in comparison with that of Cu(II)NaY catalyst. The catalytic activity was proportional to the degree of Co(II) ion exchange up to a level of about 65 to 70%. This dependence of the oxidation activity of Co(II)NaY catalyst upon cobalt(II) ion content emphasizes the importance of this exchanged cobalt(II) ion as the main active site for benzyl alcohol oxidation. The rate of formation of benzaldehyde was second order in benzyl alcohol and 0.5 order in oxygen ($r_{\phi CHO} = k \cdot [\phi CH_2OH]^2 \cdot [O_2]^{1/2}$). An activation energy of 25.6 kcal/mole was observed in the temperature range 320 to 390°C. The effect of amine addition in the Co(II)NaY catalytic system was investigated by the variation of the amount of amine addition. The addition of pyridine or piperidine increased the oxidation activity, while the addition of ethylenediamine decreased the oxidation activity. Increased concentrations of ethylenediamine resulted in the complete deactivation of Co(II)NaY catalyst for this oxidation. Cobalt(II)–pyridine or –piperidine adduct formation within the large cavities of a Co(II)NaY catalyst was demonstrated by infrared measurements. A mechanism for benzaldehyde formation over Co(II)NaY catalyst, in which dissociative oxygen species participate as a form of [Co–O], is proposed on the basis of the kinetic result obtained here. The presence of the dissociative oxygen species adsorbed on cobalt ions was suggested to contribute to the high selectivity for benzaldehyde, a partial oxidation product of benzyl alcohol.

INTRODUCTION

The catalytic work on the various zeolites have been carried out for a variety of organic reactions (*1*). The influence of the exchangeable cations on the catalytic activity of molecular sieves has been the important subject of the catalytic reaction on various forms of zeolites. Recently, the reports of the properties of the transition metal exchanged zeolites have been available. Among the transition metal ion-exchanged zeolites, copper(II)NaY zeolites have been most widely studied with respect to their structural aspects, adsorption properties, and catalytic activities (*2*). The formation and properties of copper(II)–amine complexes in Cu(II)NaY zeolites were studied by ESR measurement and gravimetric adsorption–desorption measurement (*3, 4*). Huang and Vansant (*4*) have suggested that adsorption of ammonia would pull most copper(II) ions out of the small cavities to form predominantly the four-coordinate copper–amine complex, $[Cu(NH_3)_4]^{2+}$. Further, they have reported that migration of copper(II) ions from the sodalite cages to the supercages occurred when ammonia was adsorbed. This was observed by ESR spectroscopy in conjunction with CO adsorption measurements. More recently, Lunsford (*5*) have reviewed the chemistry of transition metal complexes within the zeolites. In his valuable review, it has been demonstrated that it is possible to synthesize and characterize transition metal complexes within the zeolite cavities. Therefore, it is important to investigate the catalytic activity of transition metal complexes in zeolites with respect to the total function of zeolite, that is, to study its function as a ligand as well as its function as a solvent and anion. A variety of combinations of ligands, transition metal ions, and zeolites may be expected to develop useful catalytic application. Y-Type zeolites ion-

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exchanged with copper(II) ions have been shown to be catalysts for oxidation reactions (*6*). We have reported (*7*) benzyl alcohol oxidation over Y-type zeolite ion-exchanged with copper(II) ions; in that report, the presence of some amine has been shown to increase the catalytic activity of benzyl alcohol oxidation. It was suggested that copper(II)–amine complexes require a migration of copper(II) ions from the sodalite cages into the supercages from the oxidation activity, ESR, and ir data.

In the present work the catalytic activity of the zeolite ion-exchanged with cobalt(II) ions has been investigated in the oxidation of benzyl alcohol. The effects of cobalt(II) ion-exchanged level, reaction temperature, and calcination temperature on the activity and the selectivity of benzyl alcohol oxidation were studied. The oxidizing properties and activities of cobalt(II) ion-exchanged Y-type zeolite were attributed to the presence of cobalt(II) ions. It is of particular interest to determine the role of the cobalt(II)–amine complex in this oxidation and to compare this cobalt(II) complex with the copper(II) complex in Y-type zeolite. The Y-type zeolite ion-exchanged with cobalt(II) ions was found to have a high selectivity for partial oxidation of benzyl alcohol, though the oxidation activity was lower than that of copper(II) ion-exchanged Y-type zeolite. From the kinetic data of benzyl alcohol oxidation over Y-type zeolite ion-exchanged with cobalt ions, the reaction scheme is discussed.

EXPERIMENTAL

Catalyst preparation and materials. The starting material was Linde SK-40 (Y molecular sieve) powder. The NaY had the following properties: SiO_2, 63.5 wt%; Al_2O_3, 23.5 wt%; Na_2O, 13.0 wt%. Before the ion exchange of the NaY, it was impregnated in aqueous sodium acetate (1 M) for 2 weeks and dried at 120°C for 2 days. The cobalt(II) zeolites were prepared by treating the NaY zeolite with aqueous $Co(NO_3)_2$ at 90 to 95°C. Highly exchanged samples were prepared by repeated ion exchange. The solids were then washed in deionized water several times and dried at 120°C in an oven. The extent of ion exchange was determined by analyzing the resulting solutions for cobalt(II) by colorimetry. The cobalt(II) exchange levels were 19, 25, 34, 37, 47, 48, 59, 60, 80, and 83%.

Mean surface areas of these catalysts, measured by the BET method with N_2, were 500 to 600 m^2/g. Retention of the crystal structures of these cobalt(II) ion-exchanged Y-type zeolites, after exchange, was confirmed by the observation of the X-ray diffraction measurement (Rigaku Denki diffractometer, Model Geigerflex D-3F; Cu$K\alpha$ radiation; 2θ range of 60 to 2°). The cobalt(II) exchanged zeolites were pelleted under 400 kg/cm^2 pressure for 1 hr without a binder and crushed and sized to 20 to 32 mesh. Benzyl alcohol (guaranteed grade) was obtained from Nakarai Chemicals Company and was used without further purification. Pyridine and piperidine were obtained from Nakarai Chemicals Company and were purified by distillation. Nitrogen and oxygen were purchased commercially and were passed through silica gel before use.

Apparatus and procedure. Oxidation reactions were carried out in a fixed-bed-type reactor diluted with silica sand (2 g) with a continuous-flow system at atmospheric pressure. The reactor was 15-mm-i.d. silica tubing placed in a vertical furnace. The thermowell was located in the middle of the catalytic bed packed in the silica tube. Prior to the reaction, 0.5 g of the catalysts was heated in a mixed stream of oxygen and nitrogen (O_2/N_2 = 7/30; mole flow rate, 3.87×10^{-4} mole/sec) at 400°C for 2 hr.

Reactant and products were analyzed by means of gas chromatography, using a 10% silicone OV-17 on Chromosorb GAW DMCS for liquid products and unreacted benzyl alcohol and the intermediate cell method (*8*) with a silica gel and 5A molecular sieves for gaseous products. Details of the procedure and analysis of products and

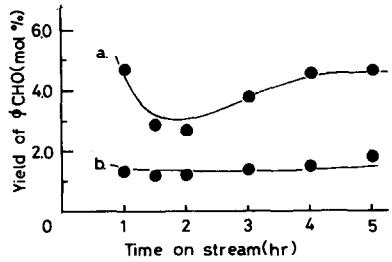

FIG. 1. Variation of benzaldehyde yield with time on stream over Co(II)NaY-34 and Co(II)NaY-80 catalysts. Reaction temperature, 370°C; catalyst, 0.5 g; W/F, 0.35 g/mol · hr^{-1}; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; pretreatment temperature, 400°C; (a) Co(II)NaY-80; (b) Co(II)NaY-34.

reactant were described in a previous paper (*7*). The conversion, yield, selectivity, and measure of contact time (W/F) have been defined previously (*7*).

Kinetic treatment. In the case of kinetic studies, the dependence of the reaction rate on partial pressure of benzyl alcohol was carried out using Co(II)NaY-59[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 0.54 g/mole · hr^{-1}. The dependence of the reaction rate on the partial pressure of oxygen was examined in a similar manner. The partial pressure of benzyl alcohol and W/F were kept constant by the variation of the partial pressure of nitrogen.

Infrared measurement. All infrared measurements were made with the catalysts in the form of self-supporting wafers prepared by pressing 20 to 40 mg of fine powder in a 20-mm-diameter die at various temperatures and various atmospheres after calcination and evacuation in an infrared *in situ* cell (NaCl windows) attached to a conventional vacuum system. Infrared spectra were recorded using a Hitachi 215 spectrophotometer.

RESULTS

The main oxidation product of benzyl alcohol oxidation over Co(II)NaY was benzaldehyde. Toluene, benzoic acid, and benzene were detected in minor quantities only at a high reaction temperature and/or a high W/F. Figure 1 shows the typical time course of the oxidation over Co(II)NaY. The reaction conditions were as follows: reaction temperature, 370°C; catalyst weight, 0.5 g; partial pressure of benzyl alcohol ($P_{\phi CH_2OH}$), 0.026 atm; partial pressure of oxygen (P_{O_2}), 0.184 atm; W/F, 0.35 g/mole · hr^{-1}. In these reaction conditions, the perfect (deep) oxidation products such as carbon monoxide and carbon dioxide were not formed, and the selectivity of benzaldehyde formation was nearly 100%. The high selectivity for the partial oxidation product (benzaldehyde) of Co(II)NaY catalyst is in contrast to that of Cu(II)NaY, a catalyst exhibiting relatively low selectivity for the partial oxidation product (*7*).

Effect of the Cobalt(II) Ions Ion-Exchanged on the Oxidation Activity

Figure 2 shows the variation of the yield of benzaldehyde as a function of percent-

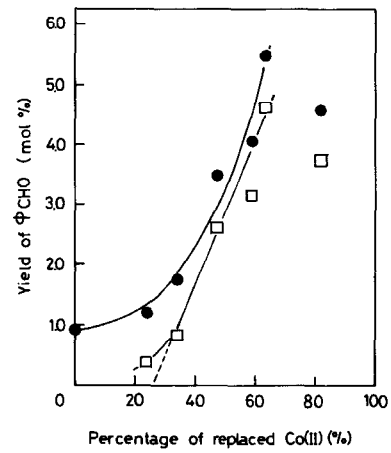

FIG. 2. Yield of benzaldehyde vs percentage of ion-exchanged cobalt(II) ions in Co(II)NaY catalyst. Reaction temperature, 370°C; catalyst, 0.5 g; W/F, 0.35 g/mole · hr^{-1}; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; pretreatment temperature, 400°C; ●, yield of benzaldehyde; □, excess yield of benzaldehyde for Co(II) catalysts over yield with NaY only.

[1] Co(II)NaY-59 refers to a Y-type zeolite in which 59% of the Na^+ cations have been exchanged by Co(II) ions.

ages of the ion-exchanged cobalt(II) ions. For the oxidation conditions employed, no other oxidation products except benzaldehyde were produced, in spite of the percentages of exchanged cobalt(II) ions used. The yield of benzaldehyde increased with the increasing percentage of the ion-exchanged cobalt(II) ions. Notably, the benzaldehyde yield increased abruptly beyond about 20% cobalt(II) ion-exchanged, whereas only a small variation was observed in the oxidation activity below 20% exchanged. Also, it is of interest to note that the yield of benzaldehyde decreased by using Co(II)NaY-83 catalyst, as shown in Fig. 2. The plots (□) obtained by subtracting the activity of NaY from that of Co(II)NaY are discussed in a later section.

Effect of the Pretreatment Temperature on the Oxidation Activity

The effect of the pretreatment temperature on the yield of benzaldehyde was examined with Co(II)NaY-80 as a catalyst. Figure 3 shows the variation of the benzaldehyde yield at 340°C. The yield of benzaldehyde increased at the higher temperatures. In the variation of pretreatment temperature, only benzaldehyde was obtained selectively as the oxidation product at 400°C. Thus it seems that the reasonable pretreatment temperature is around 400°C.

Effect of Reaction Temperature on the Oxidation Activity

The effect of the reaction temperature on benzaldehyde yield was examined with Co(II)NaY-47 as a catalyst. Figure 4 shows the variation in the yields of benzaldehyde and perfect oxidation products ($CO + CO_2$). Higher reaction temperatures increase oxidation activity but decrease selectivity for benzaldehyde. Thus carbon dioxide and carbon monoxide production become important at higher reaction temperatures. However, even in the higher reaction temperature, Co(II)NaY catalysts have the higher selectivity for the partial oxidation in comparison with Cu(II)NaY catalysts. At

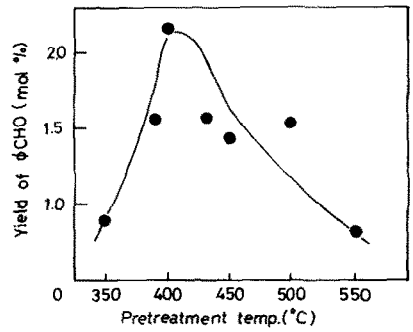

FIG. 3. Effect of pretreatment temperature on benzaldehyde yield. Catalyst, Co(II)Na-Y-80, 0.5 g; W/F, 0.35 g/mole · hr^{-1}; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; reaction temperature, 340°C; pretreatment time, 2 hr.

390°C reaction temperature, the selectivity for benzaldehyde over Co(II)NaY-47 was 85%; on the other hand 53% of the selectivity was obtained over Cu(II)NaY-19.

Kinetic Treatment

Figure 5 shows the effect of W/F on the oxidation activity over Co(II)NaY-59 at 340°C. As shown in Fig. 5, the yield of benzaldehyde increased almost linearly with the increasing W/F. Takatsu and Fujii (*9*) have reported the oxidation of benzyl alcohol over NaY catalyst. Their results indicated that increasing the W/F caused an increase in the yield of benzoic acid. However, no benzoic acid was detected for the regions of the W/F studied here.

The kinetic study for benzyl alcohol oxidation was carried out over Co(II)NaY-59 at a reaction temperature of 340°C. The dependence of the rate of the oxidation on the partial pressure of benzyl alcohol was examined by keeping the partial pressure of oxygen at 0.184 atm. The partial pressure of nitrogen was changed to keep W/F constant (0.54 g/mole · hr^{-1}). The dependence of the partial pressure of oxygen on the formation rate of benzaldehyde was also examined by a similar method. The reaction rate of the differential reactor for benzaldehyde may be generally expressed by Eq. (1):

$$r_{\phi CHO} = \Delta x/\Delta(W/F) = k \cdot P^m_{\phi CH_2OH} \cdot P^n_{O_2}, \quad (1)$$

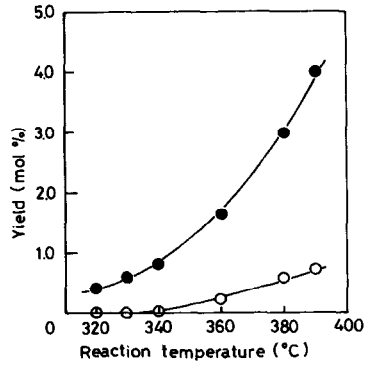

FIG. 4. Effect of reaction temperature on the oxidation activity. Catalyst, Co(II)NaY-47, 0.5 g; W/F, 0.35 g/mole · hr^{-1}; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; pretreatment temperature, 400°C; ●, ϕCHO; ○, CO + CO_2.

where k, $P_{\phi CH_2OH}$, and P_{O_2} are the rate constant and partial pressures of benzaldehyde and oxygen, respectively. Relations between log $r_{\phi CHO}$ and log $P_{\phi CH_2OH}$ or log P_{O_2} are shown in Fig. 6. Since both plots are linear, the values of m and n (the reaction orders in benzyl alcohol and oxygen, respectively) can be calculated for the formation rate of benzaldehyde. Thus the formation rate for benzaldehyde obtained experimentally is expressed by Eq. (2):

$$r_{\phi CHO} = k_e \cdot P^2_{\phi CH_2OH} \cdot P^{1/2}_{O_2}. \qquad (2)$$

An Arrhenius plot for the formation rate of benzaldehyde in the temperature range of 320 to 390°C was prepared, was shown in Fig. 7. From the slope of the straight line in Fig. 7, it was found that the apparent activation energy for benzaldehyde formation was 25.6 kcal/mole.

Effect of Amine Addition on Benzyl Alcohol Oxidation over Co(II)NaY Catalyst

The effect of amine addition on the oxidation activity of benzyl alcohol was examined using Co(II)NaY catalyst. Figure 8 shows the effects of piperidine addition over Co(II)NaY-80 at a reaction temperature of 340°C. The yield of benzaldehyde increased with the increasing addition of piperidine, but the yield of perfect oxidation products was barely detectable and increased only slightly.

Figure 9 indicates the effect of pyridine on benzyl alcohol oxidation over Co(II)NaY-80 at 340°C. The small amounts of pyridine caused an increase in the oxidation activity for benzyl alcohol. The yield of benzaldehyde increased with the increasing pyridine addition up to 6×10^{-3} of the pyridine/benzyl alcohol mole ratio. The further addition of pyridine tended to level off the yield of benzaldehyde.

Ethylenediamine is a typical chelating ligand. We have tried to use ethylenediamine as an additive for the present oxidation over Co(II)NaY. Figure 10 indicates the effect of ethylenediamine addition on benzyl alcohol oxidation over Co(II)NaY-47. As shown in Fig. 10, it is evident that the yield of benzaldehyde decreased drastically with the increasing addition of ethylenediamine; the oxidation activity was completely lost at ethylenediamine/benzyl alcohol mole ratios greater than 2.5×10^{-2}. Thus, ethylenediamine acts as an inhibitor for the reaction over Co(II)NaY-47 catalyst. Also, we have used Co(II)NaY-80 for benzyl alcohol oxidation. However, no benzaldehyde or other oxidation products were observed over Co(II)NaY-80

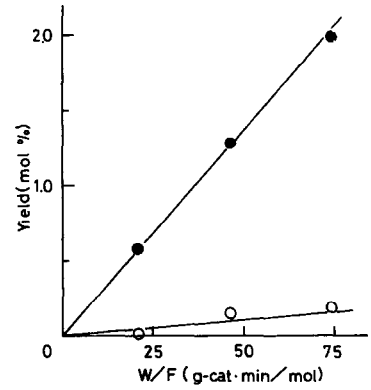

FIG. 5. Variation of the oxidation activity with increasing W/F. Reaction temperature, 340°C; catalyst, Co(II)NaY-59, 0.5 g; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; pretreatment temperature, 400°C; ●, ϕCHO; ○, CO + CO_2.

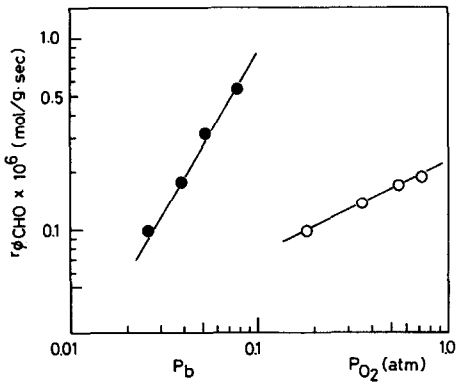

FIG. 6. Log–log plot of the formation rates of benzaldehyde vs the partial pressures of benzyl alcohol and oxygen. Catalyst, CO(II)NaY-59, 0.5 g; *W/F*, 0.54 g-cat/mole · hr^{-1}; reaction temperature, 340°C; pretreatment temperature, 400°C; ○, plots as function of O_2; ●, plots as function of ϕCH_2OH.

catalyst when the mole ratio of ethylenediamine/benzyl alcohol was 4.2×10^{-2} and the reaction temperature was 330°C.

Infrared Spectra of Co(II)NaY–Amine System

The ir spectra of pyridine adsorbed on Co(II)NaY-80 under the various measurement conditions are indicated in Fig. 11. The Co(II)NaY-80 was first evacuated for 1 hr at 300°C. Figure 11a shows the ir spectrum in which the Co(II)NaY-80 was calcined at 300°C under vacuum. The ir spectrum of pyridine adsorbed on Co(II)NaY-80 under 10 Torr at room temperature after the preliminary activation is shown in Fig. 11b. Figures 11c, d, and e show the ir spectra evacuated at various temperatures. Yoshida and his co-workers (*10*) have reported the infrared spectra of pyridine adsorbed on Co(II)NaY-48. The ir spectrum of the adsorbing pyridine at 0.5 Torr, followed by evacuation at room temperature for 15 min, has bands at 1607, 1590, 1488, and 1440 cm^{-1}. All of these bands reported by Yoshida *et al.* are observed in Fig. 11b. As shown in Fig. 11, the increasing evacuation temperature resulted in the decrease in band intensities. Particularly, the band at 1590 cm^{-1} completely disappeared at the higher evacuation temperatures. This observation is in accord with that of Yoshida *et al.*

Figure 12 shows the ir spectra obtained for a Co(II)NaY-80 sample during various stages of piperidine adsorption. Figure 12a was obtained after the Co(II)NaY-80 sample was degassed under vacuum at 300°C for 2 hr. Figure 12b shows the spectrum of the Co(II)NaY after 10 Torr of piperidine was added and then evacuated at room temperature for 15 min. The strong band at 1440 cm^{-1} and the relatively small-intensity band at 1310 cm^{-1} were observed, and the intensities of both bands decreased appreciably with increasing evacuation temperatures. These bands can be attributed to piperidine coordinated to Co(II) ions.

DISCUSSION

Oxidation Properties of the Co(II)NaY Catalyst

The main oxidation product of the benzyl alcohol oxidation over Co(II)NaY catalyst was benzaldehyde. The perfect (deep) oxidation products, carbon dioxide and carbon monoxide, were minor products, over Co(II)NaY catalyst under the reaction con-

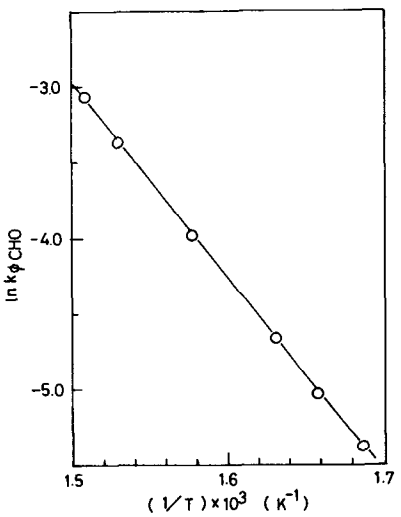

FIG. 7. Arrhenius plots for oxidation of benzyl alcohol to benzaldehyde. Catalyst, Co(II)NaY-47, 0.5 g; *W/F*, 0.35 g-cat/mole · hr^{-1}; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; pretreatment temperature, 400°C.

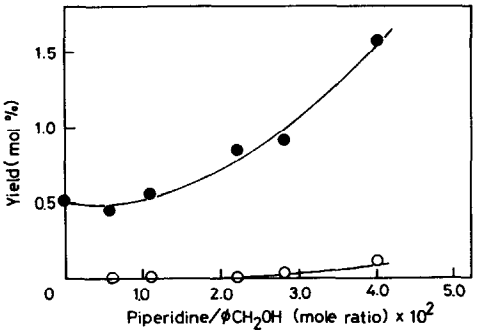

FIG. 8. Effect of piperidine addition on benzyl alcohol oxidation over Co(II)NaY catalyst. Reaction temperature, 340°C; catalyst, Co(II)NaY-80, 0.5 g; W/F, 0.35 g-cat/mole · hr^{-1}; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; pretreatment temperature, 400°C; ●, ϕCHO; ○, CO + CO_2.

ditions studied here. Thus, in contrast to the Cu(II)NaY catalyst studied previously, it was observed that the Co(II)NaY catalyst was highly selective for benzaldehyde formation in the oxidation of benzyl alcohol, although high reaction temperatures tended to cause the formation of perfect oxidation products, as shown in Fig. 4. In the oxidation of benzyl alcohol over NaY catalyst, it has been reported (*9*) that the benzaldehyde formed was oxidized to benzoic acid with increasing W/F values. However, over the Co(II)NaY catalyst, no benzoic acid was detected under the conditions of increasing contact times; instead, the yield of perfect oxidation products tended to increase with increasing contact times, as shown in Fig. 5.

The yield of benzaldehyde as a function of replaced Co(II) ion is plotted in Fig. 2 for a reaction temperature of 370°C. No deep oxidation products were yielded, and benzaldehyde was produced selectively. This observation is in contrast to that of Cu(II)NaY catalyst (*7*), over which the yield of deep oxidation products increased and the selectivity of benzaldehyde decreased with increasing percentages of replaced Cu(II) ions in the Cu(II)NaY catalyst. The yield of benzaldehyde did not increase as much with an increase in exchanged Co(II) ions for the lower exchange levels of Co(II) ions, but the yield increased almost linearly with an increase in exchanged Co(II) ions in Co(II)NaY catalyst. This observation indicates that the cobalt(II) ions in Y-type zeolite appear to be directly involved in the partial oxidation process of benzyl alcohol. The catalytic activities due to the cobalt(II) ions were calculated by subtracting the activity of NaY from that of Co(II)NaY, and the plots (□) are shown in Fig. 2. The linear plot, extraporated to zero yield, has an x-intercept at the 28% Co(II) ion-exchanged level. Thus, the activity of the exchanged Co(II) ions appeared virtually beyond the 25% Co(II) ion-exchanged level and increased almost linearly with an increase in exchanged Co(II) ions. Yoshida and his coworkers (*10*) have reported the catalytic activity of Co(II)NaY zeolite catalyst in the isomerization of 1-butene. In that reaction, the activity increased almost linearly with the increasing exchanged Co(II) ions beyond about the 5% level. However, in the present oxidation of benzyl alcohol, the yield of benzaldehyde had maximum values at about 65 to 70% of the Co(II) ion-exchanged level and tended to decrease at higher Co(II) ion contents. It has been determined that the dehydrogenation of alcohol is catalyzed by the catalyst basicity (*11*). On the other hand, the acidity of Co(II)NaY has been found to increase al-

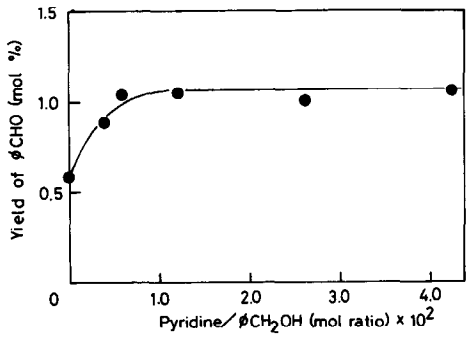

FIG. 9. Effect of pyridine addition on benzyl alcohol oxidation over Co(II)NaY catalyst. Reaction temperature, 340°C; catalyst, Co(II)NaY-80, 0.5 g; W/F, 0.35 g-cat/mole · hr^{-1}; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; pretreatment temperature, 400°C.

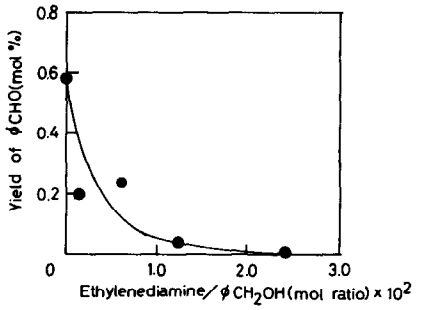

FIG. 10. Effect of ethylenediamine addition on benzyl alcohol oxidation over Co(II)NaY catalyst. Reaction temperature, 330°C; catalyst, Co(II)NaY-47, 0.5 g; W/F, 0.35 g-cat/mole · hr^{-1}; $P_{\phi CH_2OH}$, 0.026 atm; P_{O_2}, 0.184 atm; reaction temperature, 330°C; pretreatment temperature, 400°C.

most linearly with the increasing exchanged Co(II) ions to 100% of the exchange level (*10*). From these results it may be considered that the increasing exchanged Co(II) ion level promotes the oxidation activity of benzyl alcohol, but that the increase of acidity with the exchanged Co(II) ions deactivates the oxidation. These two effects in the oxidation of benzyl alcohol may combine to produce the maximum value of benzaldehyde yield, although we have no direct evidence on the basicity of the Co(II)NaY catalyst at the present time.

It was found that the yield of benzaldehyde increased with the pretreatment temperature up to 400°C, but decreased at higher temperatures, as shown in Fig. 3. Thus, the oxidation activity had a maximum value near the 400°C pretreatment temperature. A similar effect has been observed in the case of Cu(II)NaY catalyst (*7*). This observation may indicate that the excess H_2O molecules around the Co(II) ions inhibit the oxidation activity of the Co(II)NaY catalyst, but that the small amounts of H_2O are necessary for the present oxidation, as suggested in the previous paper (*7*).

Amine Effect for Co(II)NaY Catalyst

The catalytic activities of benzyl alcohol oxidation over the Cu(II)NaY–amine catalytic systems have been observed to vary with the kinds of amines and the amounts added (*7*). In the case of piperidine addition, the oxidation activity has been found to increase with the increasing addition of piperidine. On the other hand, the addition of pyridine has tended to decrease the oxidation activity with the increasing addition of pyridine. It is of interest to study the amine effect on benzyl alcohol oxidation over Co(II)NaY catalyst from two stand-

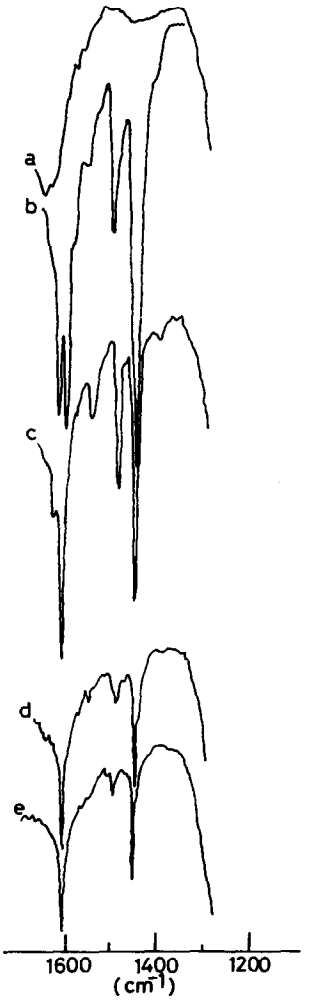

FIG. 11. Infrared spectra of pyridine adsorbed on Co(II)NaY-80. (a) Co(II)NaY-80 evacuated at 300°C for 1 hr; (b) pyridine was adsorbed at room temperature under 10 Torr and evacuated at room temperature for 15 min; (c) evacuated at 240°C for 30 min; (d) evacuated at 340°C for 1.25 hr; (e) evacuated at 360°C for 1 hr.

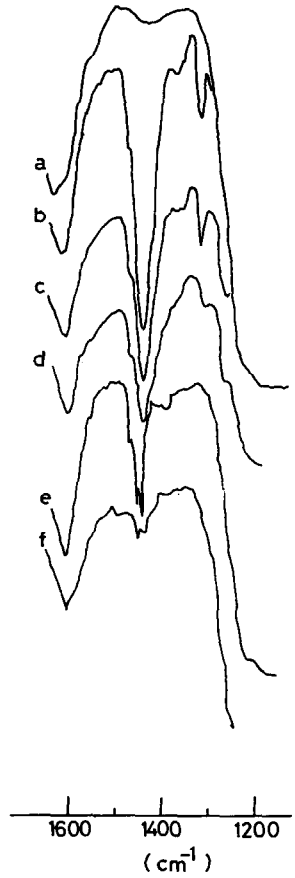

FIG. 12. Infrared spectra of piperidine adsorbed on Co(II)NaY-80. (a) Co(II)NaY-80 evacuated at 300°C for 2 hr; (b) piperidine was adsorbed at room temperature under 10 Torr and evacuated at room temperature for 15 min; (c) evacuated at 60°C for 30 min; (d) evacuated at 120°C for 30 min; (e) evacuated at 240°C for 30 min; (f) evacuated at 340°C for 1 hr.

points: (i) comparison with the amine effect over Cu(II)NaY and (ii) the possibility that cobalt(II)–amine complex catalysts introduce inhomogeneities. The addition of piperidine was found to be effective for benzyl alcohol oxidation over Co(II)NaY catalyst, as shown in Fig. 8. In this catalytic system, benzaldehyde, the partial oxidation product, was obtained almost selectively, although CO and CO_2 products tended to form with increasing mole ratios of piperidine to benzyl alcohol. In contrast with Cu(II)NaY catalyst, pyridine addition over the Co(II)NaY catalyst was found to be effective for the oxidation reaction. The small amount of pyridine caused an increase in the yield of benzaldehyde, but the yield tended to level off with the further addition of pyridine. Thus, both piperidine and pyridine additions were found to be effective for benzyl alcohol oxidation over Co(II)NaY catalyst under the present reaction conditions. It has been reported (*12*) that the Co(II) complexes with some amine ligands such as ammonia, methylamine, *n*-propylamine, and ethylenediamine are formed within the large cavities of a Co(II)NaY zeolite. For our reaction conditions, it is plausible to assume that Co(II)–amine complexes are produced within the large cavities of the Co(II)NaY zeolite, and that these Co(II)–amine complexes affect the oxidation activity of benzyl alcohol. The piperidine or pyridine adsorbed would pull the cobalt(II) ions out of the small cavities to form the corresponding Co(II)–amine complexes on the supercage, the catalytically active species for benzyl alcohol oxidation. This assumption may be confirmed from the observation of the ir spectra of piperidine and pyridine adsorbed on the Co(II)NaY catalysts. Ward (*13*) has reported that a band due to the coordinately bound pyridine appears at nearly 1446 cm^{-1} within Y-type zeolite. A band at 1448 cm^{-1} in Fig. 11 is attributed to Co(II) ion–pyridine interaction and also a band at 1440 cm^{-1} in Fig. 12 to Co(II) ion–piperidine interaction. It is worthwhile to note that the piperidine and pyridine molecules coordinated with the Co(II) ions within the Co(II)NaY catalyst are relatively stable, as is indicated from the ir spectra, even though the measurement conditions are harsh. Particularly, Co(II)–pyridine complexes formed within the Co(II)NaY catalyst seem to be more stable thermally than the corresponding piperidine complexes. In fact, the oxidation activity of benzyl alcohol tended to increase with increasing pyridine addition at 360°C. On the other hand, the addition of piperidine at the same reaction temperature had a tendency to decrease the activity.

In order to examine the effect of a potentially bidentate chelating ligand on the oxidation of benzyl alcohol at 330°C, ethylenediamine was employed. As shown in Fig. 10, the yield of benzaldehyde decreased dramatically with the increasing addition of ethylenediamine. Howe and Lunsford (*14*) have described an investigation of the oxygen adducts formed in Co(II) ion-exchanged X and Y zeolites; the low-spin $[Co(III)(en)_2O_2^-]^{2+}$ adduct is formed in the large cavities and is stable in the presence of O_2 as determined from ir, gravimetric adsorption, and ESR measurements. Under an oxygen atmosphere, it has been suggested that ethylenediamine ligand is oxidized to give imine groups. The inactivity of Co(II)–ethylenediamine complexes in the Co(II)NaY catalyst for the oxidation of benzyl alcohol may in part be associated with the oxidation of ethylenediamine ligands on exposure to oxygen. Also it may be considered that the formation of Co(II)–ethylenediamine adduct could prevent access to the benzyl alcohol molecule to the central Co(II) ions that are considered to be the active sites.

Reaction Mechanism of Benzaldehyde Formation on Co(II)NaY Catalyst

As described above, it was observed that the formation rate of benzaldehyde over Co(II)NaY-59 catalyst without amines in a fixed-bed flow reactor was second order in benzyl alcohol and 0.5 order in oxygen at 340°C. Based on the kinetic results, we propose the following mechanism as one of the plausible reaction models of benzyl alcohol oxidation over Co(II)NaY catalysts. An oxygen molecule interacts with Co(II) ions to dissociate and to give [Co–O] species, as shown in Eq. (3):

$$2[Co(v)] + O_2 \overset{K_1}{\rightleftharpoons} 2[Co\text{–}O] \quad (3)$$

$$[Co(v)] + 2[\phi\text{–}CH_2OH] \overset{K_2}{\rightleftharpoons} [Co\text{–}2\phi\text{–}CH_2OH] \quad (4)$$

$$[Co\text{–}O] + [Co\text{–}2\phi\text{–}CH_2OH] \overset{k}{\rightarrow} [Co\text{–}(\phi\text{–}CHO)(\phi\text{–}CH_2OH] + [Co(v)] \quad (5)$$

$$[Co\text{–}(\phi\text{–}CHO)(\phi\text{–}CH_2OH)] \overset{K_3}{\rightleftharpoons} [\phi\text{–}CHO] + [Co(v)] + [\phi\text{–}CH_2OH], \quad (6)$$

where

$$[Co(T)] = [Co(v)] + [Co\text{–}O] + [Co\text{–}2\phi\text{–}CH_2OH] + [Co\text{–}(\phi\text{–}CHO)(\phi\text{–}CH_2OH)]. \quad (7)$$

Co(v) is the Co(II) ion without adsorbed molecules, and Co(T) is the total cobalt(II) ions in the zeolite catalyst. It has been reported by Lunsford's group (*12*) that diatomic μ-superoxo $[L_xCo(III)O_2Co(III)L_x]^{5+}$ adducts can be formed with L = NH_3 or CH_3–NH_2, in addition to the reversible formation of low-spin $[Co(III)L_xO_2^-]^{2+}$ adducts, within the large cavities of a Co(II)NaY zeolite. Although no amine is present in the present catalytic system, it seems to be reasonable to consider a diatomic Co(II) adduct such as the dimeric Co(II) μ-superoxo complexes as a precursor of the dissociated form, [Co–O]. Equation (4) indicates the molecular adsorption of two molecules of benzyl alcohol on the active Co(II) ions in the Co(II)–NaY catalyst. Equation (5), the probable rate-determining step, shows the surface reaction of the adsorbed species on the separated active sites of the Co(II)NaY catalyst. The desorption process for benzaldehyde is shown in Eq. (6). From Eqs. (3), (4), and (6),

$$[Co\text{–}O] = K_1^{1/2} \cdot [O_2]^{1/2} \cdot [Co(v)] \quad (8)$$

$$[Co\text{–}2\phi CH_2OH] = K_2 \cdot [\phi CH_2OH]^2 \cdot [Co(v)] \quad (9)$$

$$[Co\text{–}(\phi CHO)(\phi CH_2OH)] = K_3^{-1} \cdot [Co(v)] \cdot [\phi CHO] \cdot [\phi CH_2OH]. \quad (10)$$

If Eq. (5), which is a reaction between adsorbed molecules, is assumed to be the rate-determining step,

$$r_{\phi CHO} = k \cdot \frac{[Co\text{–}O]}{[Co(T)]} \cdot [Co\text{–}2\phi CH_2OH]. \quad (11)$$

Substituting Eqs. (7), (8), (9), and (10) in Eq. (11) for the surface rate gives

$$r_{\phi CHO} = \frac{k \cdot K_1^{1/2} \cdot K_2[Co(T)] \cdot [O_2]^{1/2} \cdot [\phi CH_2OH]^2}{(1 + K_1^{1/2} \cdot [O_2]^{1/2} + K_2 \cdot [\phi CH_2OH]^2 + 1/K_3[\phi CHO]^2)^2}. \quad (12)$$

If it is assumed that K_1, $K_2 \ll 1$ and $K_3 \gg 1$, the formation rate of benzaldehyde, $r_{\phi CHO}$, is expressed as follows:

$$r_{\phi CHO} = k \cdot K_1^{1/2} \cdot K_2 \cdot [Co(T)] \cdot [\phi CH_2OH]^2 \cdot [O_2]^{1/2} \quad (13)$$

$$= k' \cdot [\phi CH_2OH]^2 \cdot [O_2]^{1/2} \quad (14)$$

where

$$k' = kK_1^{1/2} \cdot K_2[Co(T)]. \quad (15)$$

The rate expression of Eq. (*14*) is in agreement with the experimentally obtained rate law, Eq. (2), by putting $k' = k_e$.

The reaction mechanism assumed here includes dissociative oxygen species adsorbed on the cobalt ions in the Co(II)NaY catalyst. In the oxidative dehydrogenation of cyclohexane over Cu(II)NaY catalyst, Mochida and his co-workers (*6f*) have suggested that it is plausible to assume an associative oxygen species such as O_2–catalyst as the reactive species for benzene formation. Also the mechanism for benzaldehyde formation in the benzyl alcohol oxidation over Cu(II)NaY catalyst has been elucidated by the presence of the adsorbed associative oxygen on Cu(II) ions (*7*). On the other hand, Kubo and his co-workers (*15*) have studied the oxidative dehydrogenation of cyclohexane over Y-type zeolites ion-exchanged with some transition metal ions. In their paper, the metal ions of lower valence such as Fe(II) or Co(II) on Y-type zeolite were found to give fair selectivities for the cyclohexene formation, whereas metal ions of higher valence such as Cr(III) and Cu(II) on the zeolite produced no cyclohexene. They have suggested the participation of dissociative oxygen species in the cyclohexene formation of the lower-valence metal ions on the zeolite catalyst. Boudart and his co-workers (*16*) have observed the dissociative oxygen species present as the Fe–O–Fe bridge in the oxidation of ferrous ions in Y-type zeolite using Mössbauer spectroscopy and/or infrared examinations.

The remarkable stability of the 1 : 1 cobalt–oxygen adduct, $[Co(en)_2O_2]^{2+}$, in X and Y zeolites containing adsorbed ethylenediamine has been observed. Dimerization to form a 2 : 1 adduct has not been observed for oxygen adducts of Co(II)–ethylenediamine complexes in Co(II)NaY zeolite (*14*), while the corresponding dimeric cobalt–O_2–cobalt adducts have been observed in the Co(II)NaY zeolite with the ligands such as NH_3 or CH_3NH_2 (*12c*). If it is assumed that the dimeric 2 : 1 cobalt–O_2 adduct is a precursor to a dissociative oxygen species, [Co–O], as discussed above, then the relative inactivity of the co(II)NaY catalyst in the presence of ethylenediamine for the oxidation of benzyl alcohol may be related to the difficulty to form dissociative oxygen species over the catalyst. The higher selectivity for the partial oxidation product, benzaldehyde, over Co(II)NaY catalyst rather than over Cu(II)NaY catalyst seems to be attributable to the dissociative oxygen species on cobalt ions in Co(II)NaY catalyst, though we do not have direct experimental evidence of dissociative oxygen species adsorbed on cobalt ions at the present time.

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