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Ethanol Oxidation over Y-Type Zeolite Ion-Exchanged with Copper(II) and Cobalt(II) Ions

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A study was made of the gas-phase oxidation of ethanol over Cu(II) and Co(II) ion-exchanged Y-type zeolite catalysts (Cu(II)NaY and Co(II)NaY) in the temperature range 523 to 623 K in a flow system. As the oxidation product, the partial oxidation product, acetaldehyde, was formed almost selectively over both Cu(II)NaY and Co(II)NaY catalysts. From the dependence of the oxidation activity on the percentage of replaced Cu(II) or Co(II) ions, the active sites for oxidative dehydrogenation of ethanol were found to be the Cu(II) or Co(II) ions ion-exchanged by Na^+ ions in Y-type zeolite. From the kinetic studies of acetaldehyde formation over both the Cu(II)NaY and Co(II)NaY catalysts by means of a differential flow reactor, the formation rate of acetaldehyde was reciprocal first order in ethanol and one-half order with respect to the partial pressure of oxygen, irrespective of the Cu(II) or Co(II) ion-exchanged Y zeolite catalyst ($r_{CH_3CHO} = kP_{C_2H_5OH}^{-1}P_{O_2}^{1/2}$). The activation energies for the formation reaction of acetaldehyde over the Cu(II)NaY and Co(II)NaY catalysts were 70.0 and 64.7 kJ/mol, respectively, in the range 523 to 623 K. A mechanism for the formation of acetaldehyde over Cu(II)NaY and Co(II)NaY is proposed and satisfactorily agrees with the kinetic results experimentally obtained, in which the rate-determining step seems to be the surface reaction between the adsorbed ethanol and the dissociatively adsorbed oxygen.

INTRODUCTION

Considerable research efforts in the field of zeolite catalysis have been related to reactions where the zeolite is used as a solid acid, e.g., isomerization, cracking, hydrocracking. Early reports on zeolite catalysis have tended to concentrate more on the work related to acid catalysis. Lately, however, the transition metal ions and/or complexes solvated in zeolite matrices have been investigated from the point of view of the catalysis for a number of vapor-phase catalytic reactions (*1–3*). Furthermore, characterization of a variety of the transition metal ions in a zeolite framework has been accomplished through the use of different types of physicochemical measurements, such as X-ray analysis (*4*), ESR (*5–8*), NMR (*9*), electronic reflectance spectra (*10, 11*), and infrared spectra (*12–14*). In the course of these investigations, it has been clearly demonstrated that the transition metal ions located in a zeolite framework can coordinate amine, olefins, aromatics, carbon monoxide, and oxygen, and are still held to the zeolite framework by a variable number of coordinating lattice oxide ions (*5, 7, 8, 15–19*). Zeolites can effectively function both as the solvent and as the counterion (mono- to polydentate macroligand) in the formation of transition metal complexes.

So far, some investigations on the oxidation of hydrocarbon over zeolites ion-exchanged with transition metal ions have been reported (*20–25*). The mild oxidation of propene, with the incorporation of oxygen onto the organic substrate, on transition metal ion-exchanged zeolites has been the subject of important efforts, presumably due to the suitability of propene to fundamental studies of the oxidation process (*21*). Another interesting example of oxidation has been reported by Arai and Tominaga (*26*) where the ethylene was oxi-

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dized to acetaldehyde on a series of Cu(II)–Pd(II) ion-exchanged Y zeolites, which was demonstrated to be analogous to the well-known homogeneous Wacker catalyst system (*27*). It remains as an interesting example of selective oxidation using mixed transition metal ions in a zeolite matrix.

On the other hand, few studies were devoted to this dehydrogenation oxidation reaction without incorporation of the activated oxygen to the organic substrate, despite its obvious practical importance (*2*). Kazanskii and his co-workers (*16*) have reported the catalytic decomposition of ethanol on copper form of zeolite type Y, with the result that both products of the dehydrogenation and the dehydration of ethanol were formed (acetaldehyde and ethylene). In previous papers, we reported on the oxidation of benzyl alcohol over Cu(II)NaY (*28*) and Co(II)NaY (*29*) zeolites.

This work was undertaken to shed light on the reaction kinetics and the scheme which govern the formation of a partial oxidation product of ethanol over Cu(II)NaY and Co(II)NaY zeolites. Both the Cu(II) and Co(II) ion-exchanged Y-type zeolite were found to have high selectivity for the partial oxidation of ethanol under the reaction conditions studied here.

EXPERIMENTAL

Materials. The ethanol (obtained from Nakarai Chemicals Co.) was a guaranteed-grade reagent, used without purification, which was checked for purity by GLC. Nitrogen and oxygen were purchased commercially and were passed through silica gel before use.

Catalysts. Cu(II) and Co(II) ion-exchanged Y-type zeolites were prepared from a Linde NaY zeolite (SK-40) (SiO_2, 63.5 wt%; Al_2O_3, 23.5 wt%; Na_2O, 13.0 wt%) by ion exchange in a conventional manner. Ion exchange was carried out at 363–368 K with 10 wt% solutions of the appropriate salts. Cu(II) ion-exchanged Y zeolite was prepared via the chloride salt and Co(II)NaY via the nitrate salt. Retention of the crystal structure, after ion exchange, was confirmed by X-ray diffraction studies. The high exchanged level of the sample was achieved by treating the zeolite several times with the metal ion solution (*13*). The degree of ion exchange was determined by analyzing the resulting solution for the metal salts by colorimetry. All the exchanged zeolites were pelleted without a binder, crushed and sized in 20–32 mesh, and calcinated at 623 K for 2 hr before the reaction.

Apparatus and procedure. Experiments were carried out in a fixed-bed type apparatus with a continuous flow system at atmospheric pressure. The catalyst (usually 0.5 g) was placed in an electrically heated Pyrex tube reactor and calcined at a desired temperature (usually 623 K) for 2 hr in a mixed stream of oxygen and nitrogen, and then brought to the reaction temperature *in situ*. Ethanol was fed by a microfeeder. The liquid product and unreacted ethanol were cooled with a dry ice–methanol trap. The liquid sample for analysis was collected periodically. Gaseous products were collected in a 1-ml gas sampler tube connected directly to the reactor.

Analysis. The reaction mixture was analyzed by gas chromatography: for the liquid products, a 3-mm × 3-m column with Porapack Q (60–80 mesh) was used at 448 K, and for the gaseous products, with the intermediate cell method (*30*), a 40-cm column packed with silica gel (60–80 mesh) and a 2-m column packed with 5A molecular sieves (40–60 mesh) were used at 358 K. The main oxidation product was acetaldehyde. Depending upon the reaction conditions, carbon dioxide was obtained as an only minor product. The conversion of ethanol, the yield of acetaldehyde, and the selectivity of acetaldehyde were defined as follows:

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

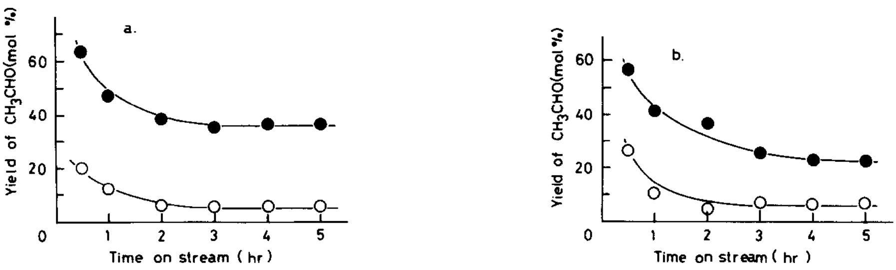

FIG. 1. Variation of acetaldehyde yield with time on stream over Cu(II)NaY and Co(II)NaY catalysts. Reaction temperature, 523 K; catalyst, 0.5 g; W/F, 1.57 × 10^3 g-cat · sec/mol; P_{EtOH}, 3.24 kPa; P_{O_2}, 18.44 kPa. (a) ●, Cu(II)NaY-67; ○, Cu(II)NaY-7. (b) ●, Co(II)NaY-59; ○, Co(II)NaY-21.

$$\text{Yield } (\%) = \frac{\text{moles of acetaldehyde produced}}{\text{moles of ethanol fed}} \times 100$$

$$\text{Selectivity } (\%) = \frac{\text{moles of acetaldehyde produced}}{\text{moles of ethanol reacted}} \times 100.$$

Kinetic treatment. For kinetic treatments, the dependence of the reaction rate on partial pressure of ethanol was investigated using Cu(II)NaY-7[1] and Co(II)NaY-21[1] as catalysts at 523 K by keeping the partial pressure of oxygen constant. The partial pressure of nitrogen was varied to keep *W/F* constant at 1.57 × 10^3 g-cat · sec/mol. The dependence of the reaction rate on the partial pressure of oxygen was examined in a similar manner. The partial pressures of ethanol and *W/F* were kept constant by variation of the partial pressure of nitrogen.

RESULTS

The oxidation of ethanol catalyzed by Cu(II)NaY and/or Co(II)NaY zeolite was performed in the temperature range 523–623 K. The only major product was acetaldehyde in both Cu(II) and Co(II) ion-exchanged Y zeolite catalytic systems. CH_4, CO, or acetic acid was not detected as the product under the present reaction conditions. Only CO_2 was detected as a minor oxidation product. The experiment in which ethanol was oxidized over Cu(II)NaY-7 catalyst at 623 K gave a CO_2 yield of only 0.09%. Thus it is reasonable to consider that both Cu(II)NaY and Co(II)NaY catalysts selectively give acetaldehyde under the reaction condition used here.

Variations in catalytic activity with time are illustrated for Cu(II)NaY and Co(II)NaY catalysts in Fig. 1. The catalytic activity decreased with the processing time. For example, in the case of Cu(II)NaY-67 (Fig. 1a), the yield of acetaldehyde is 64% at the reaction time of 30 min and decreases to ca. 40% at the reaction

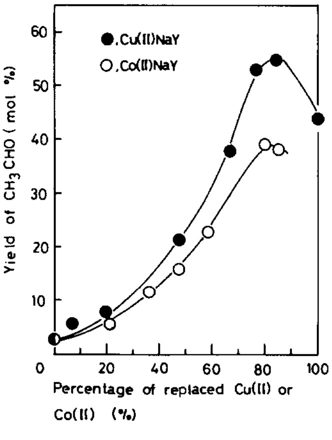

FIG. 2. Yield of acetaldehyde vs percentages of ion-exchanged Cu(II) ions in Cu(II)NaY and Co(II) ions in Co(II)NaY. Reaction temperature, 523 K; catalyst, 0.5 g; W/F, 1.57 × 10^3 g-cat · sec/mol; P_{EtOH}, 3.24 kPa; P_{O_2}, 18.44 kPa; ◐, NaY.

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[1] Cu(II)NaY-7 and Co(II)NaY-21 refer to Y-type zeolites in which 7 and 21% of the Na^+ cations have been exchanged by Cu(II) and Co(II) ions, respectively.

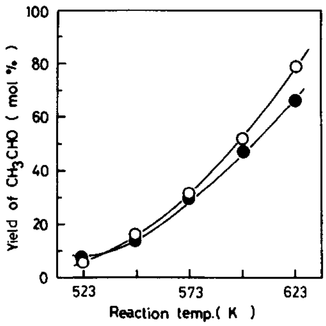

FIG. 3. Effect of reaction temperature on the yield of acetaldehyde. Catalyst, 0.5 g of Cu(II)NaY-7; W/F, 1.57×10^3 g-cat · sec/mol; P_{EtOH}, 3.24 kPa; P_{O_2}, 18.44 kPa. ○, Cu(II)NaY-7; ●, Co(II)NaY-21.

time of 3 hr. On the other hand, the selectivity of the reaction does not change with time on stream (the selectivity of acetaldehyde; 100%). A similar behavior was observed in the case of the Co(II)NaY catalyst (Fig. 1b).

Effect of the degree of the ion exchange. The yield of acetaldehyde is shown as a function of percentage of ion exchange in Fig. 2. No product other than acetaldehyde was detected in the range of ion exchange studied here. The yield of acetaldehyde increased as the percentage of exchanged Cu(II) and Co(II) ions increased. However, the yield of acetaldehyde tended to decrease at higher than ca. 80% over both Cu(II) and Co(II) ion-exchanged Y zeolites. The yield of acetaldehyde over 100% exchanged Cu(II)NaY catalyst decreased rather appreciably as shown in Fig. 2. Also it must be noted that Cu(II)NaY catalyst has a higher yield of acetaldehyde than Co(II)NaY catalyst, irrespective of the degree of the ion exchange.

Effect of reaction temperature. The effect of the reaction temperature on the yield of acetaldehyde was examined with Cu(II)NaY-7 and Co(II)NaY-21 catalysts as shown in Fig. 3. The yield of acetaldehyde monotonously increased with the reaction temperature in both the catalytic systems, and for the regions of the reaction temperatures studied here no product of the oxidation other than acetaldehyde was detected. Despite the lower degree of the ion exchange, once again, the Cu(II)NaY catalyst was found to have a higher oxidation activity than the corresponding Co(II)NaY catalyst for the regions of the reaction temperature investigated.

Effect of contact time. Figure 4 illustrates the effect of W/F on the yield of acetaldehyde over the Cu(II)NaY-7 and the Co(II)NaY-21 catalysts at 523 K. In both catalytic systems, the yield of acetaldehyde was found to increase almost linearly with increasing W/F. No other product such as acetic acid or CO_2, except acetaldehyde, was detected for the regions of the W/F studied here. Thus, from Fig. 4, it is reasonable to assume that the present reactor is taken as a differential flow reactor.

Kinetic treatment. The kinetic study for ethanol oxidation was carried out over Cu(II)NaY-7 and Co(II)NaY-21, respectively, at a reaction temperature of 523 K. The dependence of the rate of acetaldehyde formation on the partial pressure of ethanol was examined by keeping oxygen pressure at 18.44 kPa. The partial pressure of nitrogen was changed to keep W/F constant (1.57×10^3 g-cat · sec/mol). The dependence of the rate on the partial pressure of oxygen was examined in a similar manner. The partial pressures of ethanol and W/F

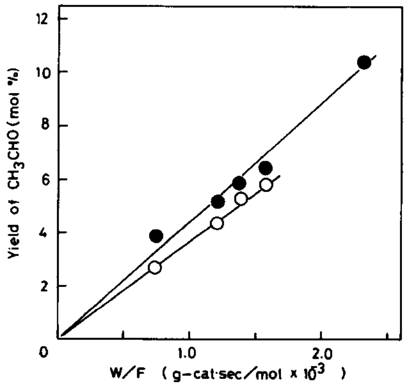

FIG. 4. Variation of acetaldehyde yield with increasing W/F. Reaction temperature, 523 K; catalyst, 0.5 g; P_{EtOH}, 3.24 kPa; P_{O_2}, 18.44 kPa. ●, Co(II)NaY-21; ○, Cu(II)NaY-7.

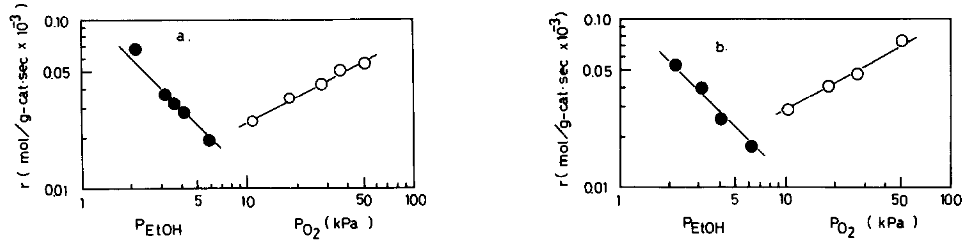

FIG. 5. Log–log plot of the formation rates of acetaldehyde vs the partial pressures of ethanol and oxygen. Reaction temperature, 523 k; catalyst, 0.5 g; *W/F*, 1.57 × 10^3 g-cat · sec/mol. (a) Cu(II)NaY-7. (b) Co(II)NaY-21; ○, plots as function of O_2; ●, plots as function of C_2H_5OH.

were kept constant at 3.24 kPa and 1.57 × 10^3 g-cat · sec/mol, respectively, for both catalytic systems. The reaction rate of the differential reactor for acetaldehyde formation could be expressed in a power form as

$$r_{CH_3CHO} = dx/d(W/F)$$
$$= \Delta x/\Delta(W/F) = k \cdot P^m_{CH_3CH_2OH} \cdot P^n_{O_2} \quad (1)$$

where k, $P_{CH_3CH_2OH}$, and P_{O_2} are the rate constant and partial pressures of ethanol and oxygen, respectively. The reaction orders m and n were determined under the partial pressure ranges shown in Fig. 5 by varying either $P_{C_2H_5OH}$ or P_{O_2} and keeping the other one constant. The relationships between log r_{CH_3CHO} and log $P_{C_2H_5OH}$ or log P_{O_2} over the Cu(II)NaY-7 and Co(II)NaY-21 are shown in Fig. 5. The values of m and n (the reaction orders in ethanol and oxygen, respectively) can be estimated for the formation rate of acetaldehyde, since both plots are linear. The formation rate equation for acetaldehyde obtained experimentally is expressed for both the Cu(II)NaY and Co(II)NaY catalytic system by

$$r_{CH_3CHO} = k \cdot P^{-1}_{C_2H_5OH} \cdot P^{1/2}_{O_2}. \quad (2)$$

Figure 6 illustrates the formation rate of acetaldehyde vs the product of $P^{-1}_{C_2H_5OH}$ and $P^{1/2}_{O_2}$ for the Cu(II)NaY catalytic system. The plots of this relationship give a straight line through the origin. Also a similar linear relationship is given for the Co(II)NaY-21 catalytic system.

Arrhenius plots for the formation rate of

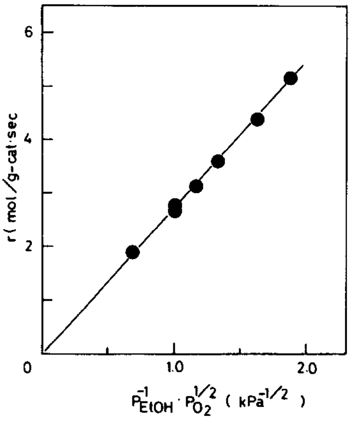

FIG. 6. Formation rates of acetaldehyde vs P^{-1}_{EtOH} · $P^{1/2}_{O_2}$. Reaction temperature, 523 K; catalyst, 0.5 g of Cu(II)NaY-7; *W/F*, 5.7 × 10^3 g-cat · sec/mol.

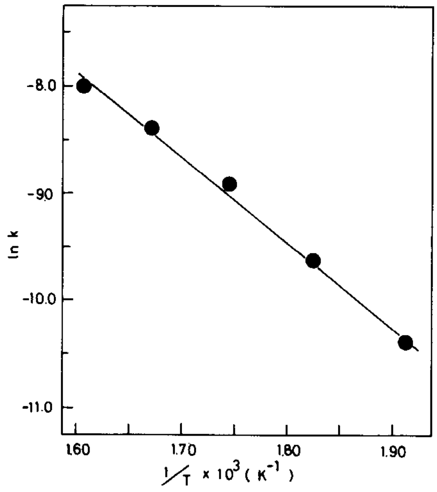

FIG. 7. Arrhenius plots for oxidation of ethanol to acetaldehyde. Catalyst, 0.5 g of Co(II)NaY-21; *W/F*, 1.57 × 10^3 g-cat · sec/mol; P_{EtOH}, 3.24 kPa; P_{O_2}, 18.44 kPa.

acetaldehyde in the temperature range 523 to 623 K are depicted in Fig. 7, in order to obtain the kinetic parameter for acetaldehyde formation. For Cu(II)NaY-7, the rate constant was

$$k = 3.186 \times 10^2 \cdot \exp(-70.7/RT) \quad (\text{mol/g-cat} \cdot \text{sec} \cdot \text{kPa}^{1/2}) \qquad (3)$$

and for the Co(II)NaY-21 system

$$k = 9.69 \times 10 \cdot \exp(-64.7/RT) \quad (\text{mol/g-cat} \cdot \text{sec} \cdot \text{kPa}^{1/2}). \qquad (4)$$

DISCUSSION

Under the reactions studied here, no product, except acetaldehyde, was detected by using both Cu(II)NaY and Co(II)NaY as the catalysts for ethanol oxidation. Thus it is reasonable to consider Cu(II) and/or Co(II) ion-exchanged Y type zeolites to have a high selectivity for partial oxidation of ethanol to form acetaldehyde. Based on the result that the yield of acetaldehyde increased with an increase in the degree of the ion exchange of Cu(II) and Co(II) ions, it seems evident that Cu(II) and Co(II) ions are active species for the formation of a partial oxidation product, acetaldehyde, though the catalytic function for the ethanol oxidation must depend on the redox ability of these two ions to alternate between two valence states. Particularly, the significant increase of the acetaldehyde yield was observed in the more than 20% of the replaced Cu(II) and/or Co(II) ions. Recently, far-infrared spectra of the zeolites HNaY at various degrees of exchange and of their dehydroxylated forms have been measured by Stock and his co-workers (*31*). The arrangement of cations in the zeolites has been studied based on the results of their far-infrared spectra, and in HNaY zeolites the concentration of Na^+ at *S*II and *S*I′ sites has been found to strongly decrease at degrees of exchange >25%. Thus the Cu(II) or Co(II) ions at sites *S*II and *S*I′ are considered to be responsible for the oxidation activity, in agreement with results by Kazanskii *et al.* (*16*), in which divalent copper ions located at sites *S*II and *S*I′ of a dehydrated zeolite of type Y are centers of adsorption of alcohol molecules. However, the maximum yield of acetaldehyde occurred when the amount of replaced Cu(II) and Co(II) ions was ca. 80%, and tended to decrease at exchange levels greater than ca. 80%. The retention of the zeolite structure in the Cu(II)NaY-100 was confirmed by direct comparison of the X-ray diffraction spectra of Cu(II)NaY-100 and NaY samples, and this means that the decrease in the yield of acetaldehyde is not due to partial destruction of the zeolite framework. A similar behavior was observed in the oxidation of benzyl alcohol over both Cu(II)NaY and Co(II)NaY (*28, 29*).

It has been reported that dehydrogenation depends on the catalyst basicity (*32*). Yashima and his co-workers have studied (*33*) the effect of additions of pyridine as a basic reagent and of phenol as an acidic reagent in the decomposition of 2-propanol over alkali cation-exchanged zeolite. Pyridine has been reported to not affect the dehydrogenation of 2-propanol. But the dehydrogenation which forms acetone as a product has been found to be almost perfectly depressed by the addition of phenol; when the addition of phenol was stopped, the dehydrogenation was slowly restored. These results by Yashima *et al.* seem to clearly show that dehydrogenation of 2-propanol was catalyzed by the basicity of the catalyst. On the other hand, the acidity of Co(II)NaY has been reported to increase almost linearly with the increasing exchanged Co(II) ions to 100% of the exchange level (*34*). The appearance of the maximum acetaldehyde yield at ca. 80% of the replaced Cu(II) or Co(II) ion might be due to the combination of the effects of both the replaced transition metal ion and the acidic sites, although we have no direct data on the acidity of the Cu(II)NaY and Co(II)NaY catalysts at the present stage. Thus an increase in the exchanged Cu(II) or Co(II) ion level promotes the oxidation activity of ethanol, but an increase in acidity with an increase in the exchanged Cu(II) or Co(II) ions depresses the formation of acetaldehyde.

The kinetic behavior of the oxidation of ethanol over both Cu(II)NaY and Co(II)NaY to selectively form acetaldehyde was found experimentally to be expressed by Eq. (2): reciprocal first order in ethanol and one-half order in oxygen molecules. Kazanskii and his group had reported earlier (*16*) that the Cu(II) ions located in sites *S*I′ and *S*II of a dehydrated Y-type zeolite are centers of adsorption of ethanol molecules, which complete the coordination sphere of Cu(II) ion to a distorted octahedron. Based on the kinetic results obtained here, we propose the following scheme as a possible reaction series for acetaldehyde formation over Cu(II)NaY and Co(II)NaY zeolite catalysts:

$$O_2 + 2M(\mathrm{v}) \overset{K_1}{\rightleftharpoons} 2M\text{–O} \quad (5)$$

$$C_2H_5OH + M(\mathrm{v}) \overset{K_2}{\rightleftharpoons} M\text{–}C_2H_5OH \quad (6)$$

$$M\text{–O} + M\text{–}C_2H_5OH \xrightarrow{k} M\text{–}CH_3CHO \quad (7)$$

$$M\text{–}CH_3CHO \overset{K_3}{\rightleftharpoons} M(\mathrm{v}) + CH_3CHO \quad (8)$$

where *M* is Cu or Co ions, and *M*(v) is the Cu or Co ions without adsorbed molecules and

$$M(\mathrm{v}) = M(\mathrm{T}) - [(M\text{–O}) + (M\text{–}C_2H_5OH) + (M\text{–}CH_3CHO)] \quad (9)$$

where *M*(T) is the total *M* ion in the zeolite catalyst.

At first a one-half order kinetic in oxygen partial pressure suggests that oxygen molecules dissociatively adsorb on Cu(II) or Co(II) to form *M*–O species (Eq. (5)). Also the adsorption of ethanol on the active Cu(II) or Co(II) ions will be considered as an initial step (Eq. (6)). Both the resultant adsorbed species on the separate active sites of the zeolite catalyst react with each other, which is considered as the rate-determining step (Eq. (7)). Equation (8) describes the desorption process of acetaldehyde formed. From Eqs. (5), (6), and (8)

$$(M\text{–O}) = K_1^{1/2} \cdot (M(\mathrm{v})) \cdot (O_2)^{1/2} \quad (10)$$

$$(M\text{–}C_2H_5OH) = K_2 \cdot (M(\mathrm{v})) \cdot (C_2H_5OH) \quad (11)$$

$$(M\text{–}CH_3CHO) = K_3^{-1} \cdot (M(\mathrm{v})) \cdot (CH_3CHO). \quad (12)$$

If Eq. (7), which is the step of the surface reaction between the adsorbed species, is assumed to be the rate-determining step

$$r_{CH_3CHO} = k \cdot (M\text{–O}) \cdot (M\text{–}C_2H_5OH). \quad (13)$$

Substituting Eqs. (9), (10), (11), and (12) in Eq. (13) for the surface rate gives

$$r = \frac{k \cdot K_1^{1/2} \cdot K_2 \cdot (M(\mathrm{T}))^2 \cdot (O_2) \cdot (C_2H_5OH)}{[1 + K_1^{1/2} \cdot (O_2)^{1/2} + K_2 \cdot (C_2H_5OH) + K_3^{-1}(CH_3CHO)]^2}. \quad (14)$$

If it is assumed that $K_2, K_3 \gg K_1$, the formation rate of acetaldehyde, r_{CH_3CHO}, is expressed as

$$r = \frac{k \cdot K_1^{1/2} \cdot (M(\mathrm{T}))^2}{K_2} \cdot \frac{(O_2)^{1/2}}{(C_2H_5OH)} \quad (15)$$

$$= k' \cdot \frac{(O_2)^{1/2}}{(C_2H_5OH)} \quad (16)$$

where

$$k' = k \cdot K_1^{1/2} \cdot K_2^{-1} \cdot (M(\mathrm{T}))^2. \quad (17)$$

The assumed reaction scheme includes dissociative oxygen adsorbed on the active sites in the zeolite. It has been reported that the fair selectivities for the cyclohexene formation of metal ions of lower valence on the molecular sieve are connected with dissociative oxygen species (*34*). On the other hand, Mochida and his co-workers have reported that it is plausible to assume associative oxygen as the reaction species for benzene formation from the oxidative dehydrogenation of cyclohexane over Cu(II)NaY zeolite, although associative as well as dissociative oxygen may be present on Cu(II)NaY (*25*). The reversible formation of low-spin $(\mathrm{Co(III)}L_x\mathrm{O_2^-})^{2+}$ adducts within the large cavities of a Co(II) ion-exchanged Y-type zeolite has been demonstrated by ESR, where $L = \mathrm{NH_3}$, $\mathrm{CH_3NH_2}$, *n*-$\mathrm{CH_3CH_2CH_2NH_2}$, and ethylenediamine, and dimeric μ-superoxo $(L_x\mathrm{Co(III)}\text{-}\mathrm{O_2^-}\text{-}\mathrm{Co(III)L_x})^{5+}$ adducts can also be formed with $L = \mathrm{NH_3}$ or $\mathrm{CH_3NH_2}$ but not with *n*-$\mathrm{CH_3CH_2CH_2NH_2}$, by Lunsford *et al.* (*1, 7, 8*). As has been reported previously (*29, 36*), the dimeric cobalt-oxygen adduct such as $L_x\mathrm{Co(II)}\text{-}\mathrm{O_2}\text{-}\mathrm{CO(II)}L_x$ might be considered as the precursor for dissociation of O_2 molecule. Using ESR spectroscopy it has been reported that the formation of copper(II) octahedral complex involving three lattice oxide ions and three oxygens from ethanol molecules was detected at *S*II sites (*16*). The formed Cu(II) complex has been found to decompose upon heating, resulting in hydrogen evolution and acetaldehyde formation. The active species in the dehydrogenation reaction has been ascribed to copper(II) ions, coordinatively unsaturated, presumably at *S*II sites, and dehydration activity has been attributed to increasing acidity upon exchange with divalent cations (*16*). From the accumulation of the data, described above, on the characterization of Cu(II) and Co(II) ion-exchanged Y-type zeolite, it seems reasonable that the Cu(II)– and Co(II)–oxygen adducts are formed as intermediates in the oxidation reaction of ethanol, although there is no amine in the zeolite cavity ion-exchanged by Cu(II) or Co(II) ions under the atmosphere of the oxidation reaction. Also, based on the results that the formation rate of acetaldehyde was dependent on one-half order in the partial pressure of oxygen, the oxygen species might be assumed to adsorb dissociatively to the Cu(II) or Co(II) ions in the zeolite at the present reaction. Although we have no definite evidence for the presence of the dissociatively adsorbed oxygen species at the present stage, the selective formation of the partial oxidation product of ethanol, acetaldehyde, may be due to the dissociatively adsorbed oxygen species, as suggested by Kubo *et al.* (*35*).

The ESR spectrum based on the Cu(II) ion of the Cu(II)NaY containing adsorbed ethanol has been observed under vacuum at the temperature of liquid nitrogen, and when the Cu(II)NaY sample has been heated, the ESR spectrum of the copper(II) ions has disappeared at 473–523 K, and at the same time, a minor amount of hydrogen gas has been found to evolve (*16*). This fact might suggest (*37*) that the one electron transfer takes place between the copper ion and the ethanol at the step of the surface reaction (Eq. (7)).

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REFERENCES

1. Lunsford, J. H., *Catal. Rev.* **12,** 137 (1975–1976).

2. Ben Taarit, Y., *in* "Catalysis by Zeolite" (B. Imelik *et al.*, Eds.), pp. 167–193. Elsevier, Amsterdam, 1980.

3. Maxwell, I. E., "Advances in Catalysis," Vol. 31, p. 1. Academic Press, New York, 1982.

4. Riley, P. E., and Seff, K., *J. Phys. Chem.* **79,** 1594 (1975).

5. Vansant, E. E., and Lunsford, J. H., *J. Phys. Chem.* **76,** 2860 (1972).

6. Martini, G., Ottaviani, M. F., and Seravalli, G. L., *J. Phys. Chem.* **79,** 1716 (1975).

7. Howe, R. F., and Lunsford, J. H., *J. Amer. Chem. Soc.* **97,** 5156 (1975).

8. Howe, R. F., and Lunsford, J. H., *J. Phys. Chem.* **79,** 1836 (1975).

9. Kazanskii, V. B., Borovkov, V. Yu., and Zhidomirov, G. M., *J. Catal.* **39,** 205 (1975).

10. Heilbron, M. A., and Vickerman, J. C., *J. Catal.* **39,** 357 (1975).

11. Sendoda, Y., Ono, Y., and Keii, T., *J. Catal.* **39,** 357 (1975).

12. Ward, J. W., *J. Catal.* **14,** 365 (1969).

13. Ward, J. W., *J. Catal.* **22,** 237 (1971).

14. Dall Betta, R. A., Garten, R. L., and Boudart, M., *J. Catal.* **41,** 40 (1976).

15. Kellerman, R., Hutta, P. J., and Klier, K., *J. Amer. Chem. Soc.* **96,** 5946 (1974).

16. Mikheikin, I. D., Pecherskaya, Yu. I., and Kazanskii, V. B., *Kinet. Catal.* **12,** 159 (1971).

17. Ben Taarit, Y., *Chem. Phys. Lett.* **62,** 211 (1979).

18. Michel, D., Meiler, W., and Pfeifer, H., *J. Mol. Catal.* **1,** 85 (1975/76).

19. Huang, Y. Y., *J. Catal.* **61,** 461 (1980).

20. Rouchaud, J., and Fripiat, J., *Bull. Soc. Chim. Fr.* **1969,** 78.

21. Mochida, I., Hayata, S., Kato, A., and Seiyama, T., (a) *J. Catal.* **15,** 314 (1969); (b) **19,** 405 (1970); (c) **23,** 31 (1971).

22. Van Sickle, D. E., and Prest, M. L., *J. Catal.* **19,** 209 (1970).

23. Rudham, R., and Sanders, M. K., *J. Catal.* **27,** 287 (1972).

24. Gentry, S. J., Rudham, R., and Sanders, M. K., *J. Catal.* **35,** 376 (1974).

25. Mochida, I., Jitsumatsu, T., Kato, A., and Seiyama, T., *J. Catal.* **36,** 361 (1975).

26. Arai, H., Yamashiro, T., Kubo, T., and Tominaga, H., *Bull. Jpn. Pet. Inst.* **18,** 39 (1976).

27. Weissermel, K., and Arpe, H. J., "Industrial Organic Chemistry." Verlag Chemie, Weinheim, 1978.

28. Tsuruya, S., Okamoto, Y., and Kuwada, T., *J. Catal.* **56,** 52 (1979).

29. Tsuruya, S., Miyamoto, H., Sakae, T., and Masai, M., *J. Catal.* **64,** 260 (1980).

30. Murakami, U., Japan Patent S 37-8447.

31. Stock, T., Dombrowski, D., Fruwert, J., and Ratajczak, H., *J. Chem. Soc. Faraday Trans. 1* **79,** 2773 (1983).

32. Tanabe, K., "Solid Acids and Bases," pp. 122, 141. Kodansha, Tokyo, 1970.

33. Yashima, T., Suzuki, H., and Hara, N., *J. Catal.* **33,** 486 (1974).

34. Yoshida, S., Nakajima, M., Naito, K., Koshimizu, Y., and Tarama, K., *Bull. Inst. Chem. Res. Kyoto Univ.* **52,** 567 (1974).

35. Kubo, T., Tominaga, H., and Kunugi, H., *J. Chem. Soc. Jpn.* **44,** 2595 (1971).

36. Naccache, C., and Taarit, Y. B., *in* "Zeolites: Science and Technology" (F. R. Ribeiro, A. E. Rodrigues, L. D. Rollmann, and C. Naccache, Eds.), p. 373. Martinus Nijhoff Publishers, Hague, 1984.

37. Hall, W. K., Private communication.