

Catalysis of Cu(II)-NaZSM-5 Zeolites during Benzyl Alcohol Oxidation

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The vapor-phase oxidation of benzyl alcohol over copper(II) ion-exchanged NaZSM-5 type zeolites (Cu(II)-NaZSM-5) was studied. The major products were benzaldehyde and carbon oxides (CO₂ + CO). The Cu(II)-NaZSM-5 catalysts showed higher catalytic activity for benzyl alcohol oxidation than the corresponding Y type zeolites. The influence of reaction temperature and the degree of Cu(II) ion exchange on the catalytic activity and the selectivity in the benzyl alcohol oxidation was investigated. From the kinetic results, the formation rate of benzaldehyde was found to be first order with respect to the partial pressure of benzyl alcohol and the reciprocal of first order with respect to the partial pressure of oxygen. The Cu(II) ions in the Cu(II)-NaZSM-5 zeolites were found to be easily reduced by degassing at higher temperatures. On the basis of the IR spectra of benzyl alcohol adsorbed on the Cu-NaZSM-5 zeolites, which were treated under oxidizing and/or reducing atmospheres, the oxidation of benzyl alcohol to benzaldehyde was suggested to proceed by the one-electron redox process of the copper ions. A reaction scheme is proposed in which the Cu(II) ion and/or Cu(II)-O₂⁻ adduct in the NaZSM-5 zeolite seem/seems to react with benzyl alcohol adsorbed on the Cu(II) ion to give benzaldehyde and the Cu(I) ion, which is rate-determining. The reduced Cu(I) ion can be readily reoxidized to the Cu(II) ion by molecular oxygen.

Introduction

Catalysis by transition metal ions and/or their complexes has mainly been reported for homogeneous liquid-phase systems, which are usually found to be more selective and to have better reproducibilities in catalytic reactions than heterogeneous catalysts. Even with these advantages, homogeneous metal complex catalysts have not been widely used as commercial catalysts, because their recoveries by separation from the reactants and the products are difficult and result in considerable loss of expensive metal catalyst.

Zeolite has been known to behave as a "solid solvent" and has led to a new class of catalysts because of their content of exchange cations. The formation of transition metal complexes in zeolites has been an interesting area of investigation. Extensive studies of transition metal ion-exchanged zeolites have been performed concerning their structural aspects, adsorption properties, and catalytic activities.¹⁻³ Copper ions in faujasite type zeolite have been extensively studied with regard to the sites of the copper ion, their influence on the adsorption properties, and the role which the copper ions play in catalysis. In addition to using zeolite as a solid acid catalyst such as one for cracking reactions, considerable research in the field of zeolite catalysis has focused on the catalysis of transition metal ion-exchanged zeolites in reactions generally catalyzed by metal ions in solution.⁴⁻⁸ We have studied⁹⁻¹¹ benzyl alcohol and ethanol oxidations over copper ion- and cobalt ion-

exchanged Y type zeolites and have demonstrated that the active sites for the oxidation of these alcohols to corresponding aldehydes were transition metal ions in the zeolite framework. The addition of amines such as pyridine and piperidine would pull the metal ions out of the sodalite cages and thereby increases the number of accessible metal ions, which would lead to an increase in aldehyde yield. Although much work has been devoted to the study of copper ions in faujasite type zeolites, more recently studies of the nature and the redox behavior of copper ions in NaZSM-5 type zeolites have been reported.²⁴

The present contribution reports a study on the catalysis of Cu(II)-NaZSM-5 (Cu(II)-NaZ) zeolites in benzyl alcohol oxidation and focuses on the redox properties of copper ions in NaZSM-5 zeolites during the oxidation. The characteristic that cupric ions are easily reduced to cuprous ions in NaZSM-5 zeolite compared with faujasite type zeolites is emphasized in this study.

Experimental Section

Catalysts. NaZSM-5 zeolite was prepared as described in a patent.¹² Tetrapropylammonium bromide was used as the organic template. The zeolite was calcined at 773 K for 5 h in air to remove organic residues in the zeolites before further use. After the calcined zeolite was washed with boiled deionized water for 2 h, the zeolite was immersed in 1 N NaNO₃ aqueous solution for 1 h at 345-353 K, which was repeated twice. The NaZSM-5 zeolite formed was once again calcined at 773 K for 5 h in air. The crystallinity of the synthesized NaZSM-5 zeolite was ascertained by powder X-ray diffraction (Rigaku Model 2122-B-3 diffractometer). The sample was distributed on a glass slide and examined with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The Si/Al atomic ratio of the NaZSM-5 was found to be 35 from measurements using an atomic absorption spectrophotometer (Shimadzu Model AA-630-01). Copper(II) ion-exchanged NaZSM-5 zeolite was prepared by ion exchange in the conventional manner, at 358 K with an aqueous solution of copper(II) acetate (pH 5.82-5.85). The Cu(II)-NaZSM-5 zeolite obtained was dried at 393 K overnight in air and calcined at 773 K for 5 h in flowing air. The degrees of ion exchange of copper(II) and sodium ions were determined by analyzing homogeneous solutions of Cu(II)-NaZSM-5 (Cu(II)-NaZ) dissolved in hydrogen fluoride with an atomic absorption spectrophotometer (Shimadzu Model AA-630-01). The ratios of the Cu(II) ions exchanged vs the sodium ions removed were confirmed to nearly equal 2. The catalyst was designated Cu(II)(x)-NaZ, where x is the degree of ion exchange of Cu(II) ions.

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Gas-Phase Catalytic Oxidation of Benzyl Alcohol over Cu(II)-NaZ.

The oxidation reaction was carried out in a fixed-bed type vertical reactor under a continuous gas flow at atmospheric pressure. The catalyst (0.5 g) was packed in a Pyrex tube reactor which was placed in an electrically heated furnace, calcined at 773 K for 2 h in a mixed stream of oxygen and nitrogen (O_2/N_2 mole ratio 7/30; total mole flow rate 3.87×10^{-4} mol/s), and then brought to the reaction temperature, which was monitored by a thermocouple located in the middle of the reactor tube. Benzyl alcohol was obtained from Nakarai Chemicals Co. as a guaranteed grade reagent and was used without further purification after being checked for impurities by GLC. The reactant was fed by a microfeeder. Unreacted reactant and liquid products were collected in a trap maintained at 251 K (CCl_4 + liquid N_2) and analyzed by a Shimadzu Model GC-6A gas chromatograph. The chromatograph was equipped with a flame ionization detector using a 0.3-cm-i.d. by 3-m-length stainless-steel column packed with 10% silicone OV-17 on Chromosorb GAW DMCS support maintained at 473 K with nitrogen as a carrier gas ($0.37 \text{ cm}^3/\text{s}$). Gaseous products were collected in a 1-cm³ gas sampler tube connected to the reactor. The gaseous products were analyzed by means of gas chromatography (Gas-Chrokyo Model KOR-1) with the intermediate-cell method¹³ using a 1 m \times 0.3 cm stainless-steel column packed with silica gel (60–80 mesh) maintained at 393 K and a 3 m \times 0.3 cm stainless-steel column packed with 5-Å molecular sieves (80–100 mesh) at 293 K with hydrogen as a carrier gas ($0.37 \text{ cm}^3/\text{s}$). The main oxidation products were benzaldehyde and carbon oxides ($CO_2 + CO$). Depending upon the reaction conditions, only trace amounts of benzene and toluene were obtained as minor products.

IR Spectra of Gases Adsorbed on Cu(II)-NaZ Zeolite. All IR spectra were obtained using an Analect Instrument Model FX-6200 FT-IR spectrophotometer and were recorded between 1300 and 2300 cm^{-1} after cooling the samples to room temperature. These measurements were carried out in an in-situ infrared cell which allowed pretreatment. The samples were compressed at 400 kg/cm^2 for 10 min into thin wafers weighing ca. 20 mg. The diameter of each disk was ca. 20 mm.

Adsorption Measurement of CO Adsorbed on Cu(II)-NaZ Zeolite. CO adsorption was achieved using a setup consisting of a conventional low-pressure static type gas adsorption system. Prior to each experiment, the catalyst was pretreated at 773 K under 150 Torr of O_2 for 1 h, followed by degassing under less than 2×10^{-4} Torr at 773 K for 2 h. CO was adsorbed at room temperature until adsorption equilibrium was reached.

ESR Measurements of Cu(II)-NaZ Zeolites. ESR measurements of catalyst samples, pretreated at 673–773 K under O_2 , CO, and vacuum for 2 h, respectively, and placed in 3-mm-o.d. quartz tubes, were carried out at room temperature at X-band on a JEOL Model JES-PE spectrometer.

Results**Catalytic Activity of Cu(II)-NaZ in Benzyl Alcohol Oxidation.**

The conversion of benzyl alcohol oxidation without the Cu(II)-NaZ catalyst was negligible at temperatures lower than 673 K. The yields of benzaldehyde and carbon oxides ($CO_2 + CO$) in benzyl alcohol oxidation by Cu(II)(70)-NaZ are illustrated as a function of time on stream in Figure 1. Both the yields catalyzed by Cu(II)-NaZ were constant through process times of at least 5 h, in contrast to those for the Cu(II)-NaY catalyst,^{9,11} which exhibited a sharp decrease in yields at early stages of time on stream. The specific micropore structures of ZSM-5 type zeolites have been reported to have an extremely high resistance to coke deposition, compared with the supercages of Y type zeolites, on which carbonaceous products are easily formed without limitation by steric constraints.^{14–17} All other Cu(II)-NaZ catalysts used here were found to have yield vs process time relationships similar to those for the Cu(II)(70)-NaZ catalyst.

The influence of reaction temperature on both the yields of benzaldehyde and carbon oxides was examined with Cu(II)(70)-

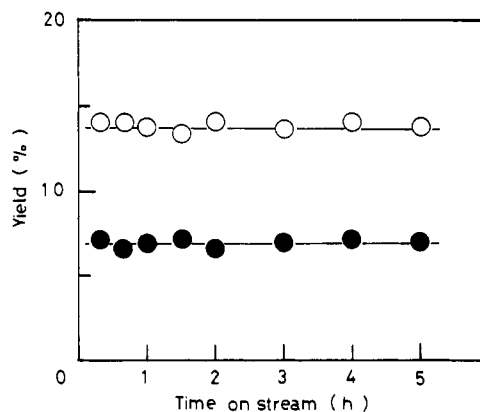


Figure 1. Variation in benzaldehyde and carbon oxide yields with time on stream over Cu(II)(70)-NaZ catalyst (reaction temperature 673 K): ●, benzaldehyde; ○, carbon oxide.

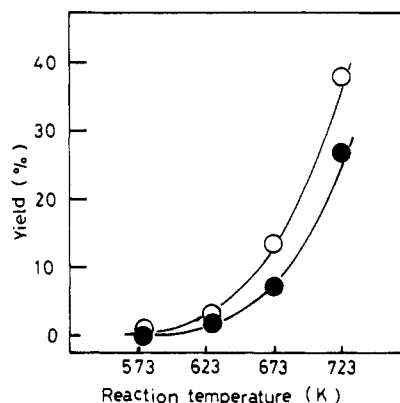


Figure 2. Effect of reaction temperature on benzaldehyde and carbon oxide yields (catalyst Cu(II)(70)-NaZ): ●, benzaldehyde; ○, carbon oxide.

Table I. Effect of Reaction Temperature on the Conversion and Yields in the Benzyl Alcohol Oxidation by Cu(II)-NaZ^a

T (K)	conversion (%)	yields (%)	
		benzaldehyde	CO ₂ + CO
573	1.1	0.1	1.0
623	4.5	1.5	3.0
673	20.5	7.0	13.5
723	65.0	27.0	38.0

^a Catalyst: Cu(II)(70)-NaZ, 0.5 g. $W/F = 1.34 \times 10^3$ g of catalyst \cdot s \cdot mol⁻¹; $P_{\text{PrCH}_2\text{OH}} = 3.20 \times 10^3$ Pa; $P_{O_2} = 1.11 \times 10^4$ Pa; $P_{N_2} = 8.7 \times 10^4$ Pa.

NaZ zeolite, as shown in Figure 2 and Table I. Both the yields sharply increased at around 623 K. The selectivity of the partial oxidation product, benzaldehyde, was considerably high even at higher reaction temperatures. A comparison of the selectivities in only one conversion value must be pointed out to be dangerous, since both the yields change tremendously with conversion, as seen in Table I.

Both the yields of benzaldehyde and carbon oxides ($CO_2 + CO$) are shown as a function of the degree of the Cu(II) ion exchange in Figure 3. The yield of carbon oxides increased with an increasing percentage of Cu(II) ions. The yield of benzaldehyde gradually increased with an increase in the degree of the Cu(II) ion exchange and abruptly increased beyond about 50% Cu(II) ion exchange, though the benzaldehyde yield inversely tended to decrease with further increased Cu(II) ion exchange.

The variation in the yields of both benzaldehyde and carbon oxides as a function of time on stream was immediately observed when the oxygen supply was stopped after the steady-state yields of benzaldehyde and carbon oxides were obtained under an oxygen atmosphere (Figure 4). The yields of carbon oxides ($CO_2 + CO$)

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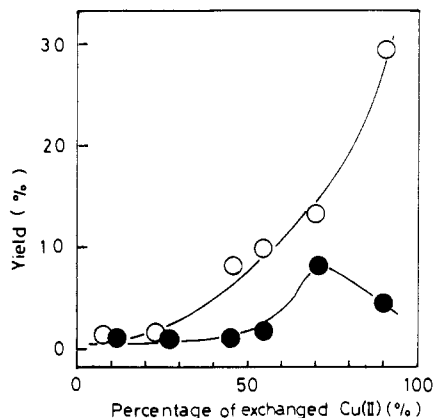


Figure 3. Yields of benzaldehyde and carbon oxides vs percentages of ion-exchanged Cu(II)-NaZ (reaction temperature 673 K): ●, benzaldehyde; ○, carbon oxide.

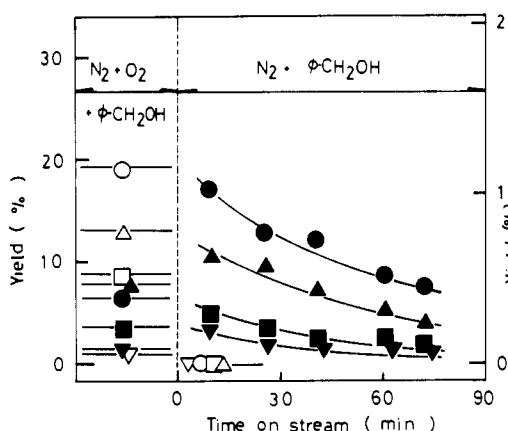


Figure 4. Oxidation behavior of Cu(II)-NaZ under N_2 atmosphere: ●, ○, Cu(II)(89)-NaZ; ▲, △, Cu(II)(70)-NaZ; ■, □, Cu(II)(45)-NaZ; ▼, ▽, Cu(II)(26)-NaZ; ●, ▲, ■, ▼, benzaldehyde; ○, △, □, ▽, carbon oxide.

immediately dropped to zero after the oxygen supply was stopped, regardless of the percentages of the Cu(II) ion exchange. In contrast to carbon oxides, benzaldehyde was observed even in the absence of oxygen, though the yields were considerably low in comparison with the yields obtained in the presence of oxygen. The yields of benzaldehyde, which were on the order of the degree of Cu(II) ion exchange of the Cu(II)-NaZ catalysts, decreased with decreasing process time. The formation of benzaldehyde may be due to the depletion of the oxygen species which was retained on the Cu species in the zeolites during the steady-state process in the presence of oxygen.¹⁸

The effect of the pretreatment with CO and H_2 at 773 K for 1 h on the yield of benzaldehyde was examined under a nitrogen atmosphere using Cu(II)(70)-NaZ zeolite. Before the pretreatment, as mentioned previously, each catalyst was calcined under oxygen at 773 K for 2 h. The initial yield of benzaldehyde over the Cu(II)(70)-NaZ pretreated only by calcination was higher than those over the Cu-zeolites pretreated with CO and H_2 , though the benzaldehyde yields over the former catalytic system for longer times on stream became almost similar to those with the latter two catalytic systems.

Kinetics of the Formation of Benzaldehyde in Benzyl Alcohol Oxidation. A kinetic study was carried out over the Cu(II)(70)-NaZ catalyst at a reaction temperature of 673 K. The yield of benzaldehyde increased almost linearly with an increase in W/F (W = weight of catalyst; F = total flow rate), a measure of contact time, in the regions of 7.2×10^2 – 2.2×10^3 g of catalyst-s/mol. Thus the principle of a differential reactor could be applied. The reaction rate of the differential reactor for benzaldehyde

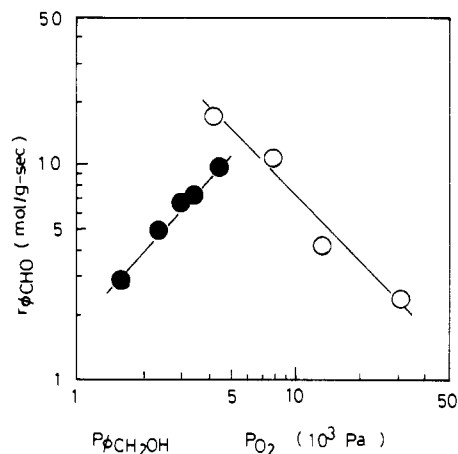


Figure 5. log-log plot of the formation rate of benzaldehyde vs the partial pressures of benzyl alcohol and oxygen (catalyst Cu(II)(70)-NaZ; reaction temperature 673 K): ●, plots as function of benzyl alcohol ($P_{O_2} = 11.1$ kPa); ○, plots as function of O_2 ($P_{PhCH_2OH} = 3.2$ kPa).

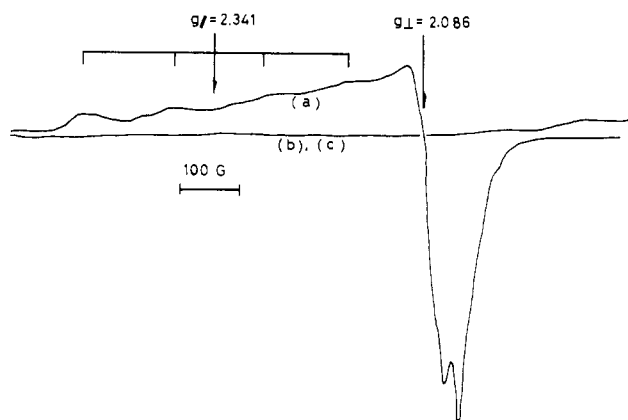


Figure 6. ESR spectra of Cu(II)(70)-NaZ at room temperature: (a) calcined at 773 K for 2 h under O_2 (150 Torr); (b) reduced at 573 K for 2 h under CO (150 Torr); (c) Degassed (less than 2×10^{-4} Torr) at 773 K for 2 h.

may be generally expressed by eq 1, where k , P_{PhCH_2OH} , and P_{O_2}

$$r_{PhCHO} = \Delta x / \Delta(W/F) = k P_{PhCH_2OH}^m P_{O_2}^n \quad (1)$$

are the rate constant and partial pressures of benzyl alcohol and oxygen, respectively. Relationships between $\log r_{PhCHO}$ and $\log P_{PhCH_2OH}$ and P_{O_2} are shown in Figure 5. From the slopes of the straight lines shown in Figure 5, the formation rate of benzaldehyde (r_{PhCHO}) was found to be first order with respect to the partial pressure of benzyl alcohol and the reciprocal of first order with respect to the partial pressure of oxygen (the slopes in Figure 5, calculated by the least-squares method, were 1.16 and -1.03, respectively). The rate describing the oxidation is thus expressed in the form of eq 2. Arrhenius plots for the formation rate of

$$r_{PhCHO} = k P_{PhCH_2OH} P_{O_2}^{-1} \quad (2)$$

benzaldehyde in the temperature range 573–723 K were prepared for the Cu(II)(70)-NaZ catalyst in order to obtain the apparent activation energy. This was calculated to be 37.4 kJ/mol, and the exponential factor, to be 217 mol/h.

Electron Spin Resonance Spectra of Cu(II)(70)-NaZ Zeolite. ESR was used to monitor the oxidation states of copper ions in NaZSM-5 zeolite during CO treatment and degassing at high temperature. Figure 6a illustrates the ESR spectrum of the Cu(II)(70)-NaZ catalyst pretreated under an oxygen atmosphere (150 Torr) at 773 K for 2 h, in which the ESR peaks of more than one type of Cu(II) ion are superimposed on each other. The

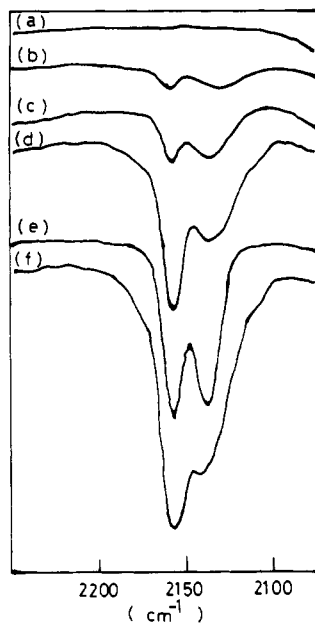


Figure 7. IR spectra of CO adsorbed on Cu(II)-NaZ catalyst (Pre-treatment, degassed at 773 K for 2 h; CO adsorption, 50 Torr of CO exposed for 5 min followed by evacuation at room temperature for 5 min): (a) Cu(II)(9)-NaZ; (b) Cu(II)(26)-NaZ; (c) Cu(II)(45)-NaZ; (d) Cu(II)(54)-NaZ; (e) Cu(II)(70)-NaZ; (f) Cu(II)(89)-NaZ.

Cu(II) signal with $g_{\parallel} = 2.341$ ($A_{\parallel} = 151.6$ G) and $g_{\perp} = 2.086$ is typical of an anisotropic Cu(II) ion, through the absorption peaks of the other Cu(II) species were not identified because of their poor resolution. It is clear that the treatment of Cu(II)(70)-NaZ with CO at 573 K or the degassing (less than 2×10^{-4} Torr) at 773 K of the zeolite caused a dramatic reduction of the Cu(II) species in NaZ, as shown in Figure 6b,c. The ESR results suggest that the Cu(II) species in the NaZ zeolites are easily reduced during both CO treatment and degassing at high temperature.

Infrared Spectra of CO Adsorbed on Cu(II)-NaZ. To study the redox properties of the copper species in the Cu(II)-NaZ zeolite, the IR spectra of Cu-NaZ zeolites treated with carbon monoxide or degassed at various temperatures were recorded. The presence of Cu(I) ions has been probed by using carbon monoxide adsorption and examining the specific interaction with IR spectroscopy.¹⁹⁻²² The IR spectra of CO adsorbed on the Cu-NaZ zeolites, in which the degree of Cu ion exchange was varied from 9% to 89%, evacuated at 773 K for 2 h, are illustrated in Figure 7. Two absorption bands were observed at 2135 and 2157 cm^{-1} when CO at 50 Torr was introduced at room temperature. They persisted even after the CO gas had been pumped off to ca. 2×10^{-4} Torr at room temperature for 5 min (Figure 7). It is clear that the intensities of these bands increase with increased degree of Cu ion exchange. Nicol and Howard²² reviewed the characterization of Cu(I) in Y zeolites by FT-IR absorption and carbon monoxide adsorption. The bands at 2156, 2147, and 2127 cm^{-1} have been assigned to Cu(I)-CO complexes in a different framework location in the Y zeolite.²² Two peaks at 2157 and 2135 cm^{-1} , which were observed in the IR spectra of CO-adsorbed Cu-NaZ degassed at 773 K, can be assigned to the Cu(I)-CO species. The Cu(II) ions in the NaZ zeolite were thus found to be easily reduced to Cu(I) ions by degassing Cu-NaZ at 773 K. This reduction of Cu(II) to Cu(I) ions may accompany deoxygenation from the zeolite framework as suggested by Jacobs et al.¹⁹

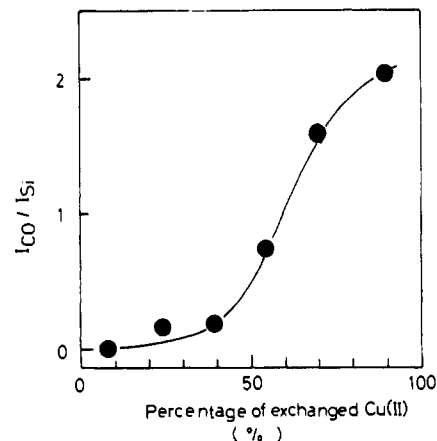


Figure 8. Relative amount of adsorbed CO vs degree of ion-exchanged Cu(II) (I_{Si} = intensity of the 2007- cm^{-1} band; I_{CO} = total intensity of the 2157- and 2135- cm^{-1} bands).

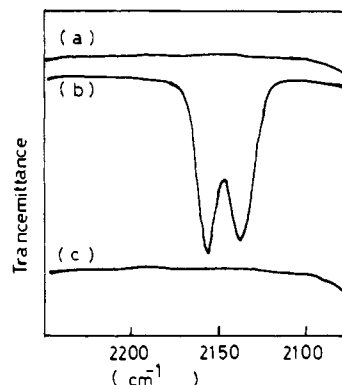


Figure 9. Redox behavior of Cu(II)(70)-NaZ observed from IR spectra of adsorbed CO: (a) calcined at 773 K for 2 h under O_2 followed by exposure to 50 Torr of CO at room temperature for 5 min and degassing at room temperature for 5 min; (b) degassing at 773 K for 2 h after (a) followed by exposure to 50 Torr of CO for 5 min and degassing for 5 min; (c) calcined at 773 K for 2 h under O_2 followed by exposure to 50 Torr of CO for 5 min and degassing for 5 min.

The ratio of the total intensity (I_{CO}) of the 2157- and 2135- cm^{-1} bands to the intensity (I_{Si}) of the 2007- cm^{-1} band, which is due to Si in the zeolite framework, was plotted for the degree of the Cu(II) ion exchange as shown in Figure 8. The ratio I_{CO}/I_{Si} is considered to be the relative intensity of the Cu species which were reduced to Cu(I) ions through the evacuation at 773 K. The reducible Cu(II) ion abruptly increased beyond about 40-50% Cu(II) ion exchange, whereas comparably slight reductions to Cu(I) ions were observed below 40% exchange.

The mole ratios of the amounts of CO adsorption to Cu ions ion-exchanged in Cu-NaZ, which was degassed at 773 K for 2 h after calcination at 773 K for 1 h under O_2 (150 Torr), were found to increase with an increase in the degree of the Cu(II) ion exchange. This result may suggest that more than one class of Cu species, the redox properties of which are different from each other, is present in the Cu-NaZ zeolites, in agreement with the results of the IR measurement for CO adsorbed on Cu-NaZ zeolites (Figure 8).

The redox properties of the Cu species in the NaZ zeolite were studied with IR spectra of CO adsorbed on Cu-NaZ. Figure 9 illustrates the variation in the IR spectra of CO adsorbed on Cu-NaZ during oxygen treatment. No IR absorption peaks were observed for CO adsorbed on Cu-NaZ treated under an oxygen atmosphere at 773 K for 2 h (Figure 9a). Two absorption peaks at 2157 and 2135 cm^{-1} appeared when CO was adsorbed on the sample after the sample of Figure 9a was degassed at 773 K for 2 h (Figure 9b). The IR absorption peaks based on CO adsorbed on the Cu(I) species (Figure 9b) disappeared when the sample

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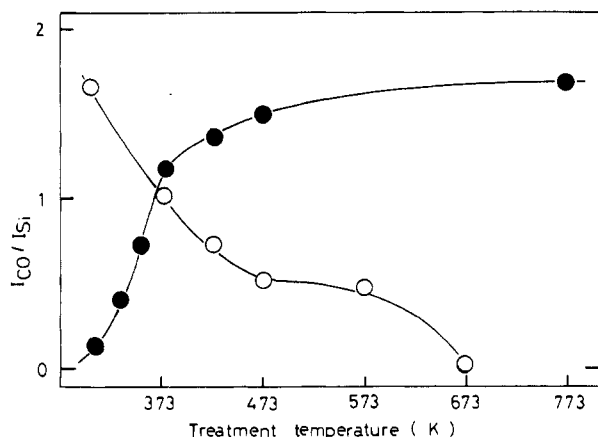


Figure 10. Variation in relative amount of adsorbed CO with pretreatment temperature (I_{Si} = intensity of the 2007- cm^{-1} band; I_{CO} = total intensity of the 2157- and 2135- cm^{-1} bands; catalyst Cu(II)(70)-NaZ); ●, calcined at 773 K for 2 h under O_2 followed by degassing at the prescribed temperature for 1 h; ○, degassed at 773 K for 2 h followed by exposure to 100 Torr of O_2 at the prescribed temperature for 1 h and exposure to 50 Torr of CO at room temperature for 5 min and degassing at room temperature for 5 min.

of Figure 9b was once again treated under an oxygen atmosphere at 773 K for 2 h (Figure 9c). This means that Cu(I) species reduced through evacuation at high temperature were reoxidized to the Cu(II) species through oxygen treatment.

The relationships of I_{CO}/I_{Si} vs degassing temperature and oxygen treatment temperature are plotted as shown in Figure 10 to illustrate the redox properties of the Cu species in Cu(II)(79)-NaZ zeolite. The relative intensity, I_{CO}/I_{Si} , which is a measure of the amount of the reduced Cu(I) species, increased with increasing temperature of the degassing treatment up to ca. 473 K and then reached almost a plateau. These results, together with the ESR results (Figure 6) mentioned previously, may suggest that most of the Cu(II) ions in Cu(70)-NaZ are reduced to Cu(I) ions through degassing at a temperature higher than ca. 473 K. I_{CO}/I_{Si} decreased with an increase in temperature of oxygen treatment of Cu(70)-NaZ, which was previously reduced by degassing at 773 K, and I_{CO}/I_{Si} became zero at around 673 K. All the Cu(I) ions in the NaZ zeolite were found to be oxidized to Cu(II) ions with oxygen treatment at temperatures higher than 673 K.

Infrared Spectra of Benzyl Alcohol Adsorbed on Cu-NaZ Zeolites. The IR spectra of benzyl alcohol adsorbed on the zeolites after various pretreatments of the Cu-NaZ zeolites are shown in Figure 11. An absorption band at 1694 cm^{-1} was observed when benzyl alcohol was adsorbed at room temperature on Cu(70)-NaZ which was pretreated at 773 K under an oxygen atmosphere for 2 h, as shown in Figure 11b,c,d. The absorption band at 1694 cm^{-1} is identified as the stretching band of the carbonyl group of adsorbed acetaldehyde. The intensity of this band tended to increase with time. In contrast to the spectrum of the oxygen-treated Cu(70)-NaZ catalyst described above, no absorption band appeared around 1700 cm^{-1} when benzyl alcohol was introduced to the Cu(70)-NaZ catalyst evacuated at 773 K for 2 h (Figure 11g). No absorption band at 1694 cm^{-1} was observed when ethanol was adsorbed on a low Cu(II) ion-exchanged NaZ zeolite (Cu(II)(9)-NaZ) pretreated under an oxygen atmosphere at 773 K for 2 h (Figure 11f).

Figure 12a illustrates the IR spectrum of benzyl alcohol adsorbed at room temperature on Cu(70)-NaZ after preliminary evacuation at 773 K, followed by allowing it to stand at 373 K for 1 h under 350 Torr of He. Benzyl alcohol was adsorbed at room temperature on Cu(70)-NaZ calcined at 773 K for 2 h under oxygen, and the whole system was followed by allowing it to stand at 373 K for 1 h under He (350 Torr). On introduction

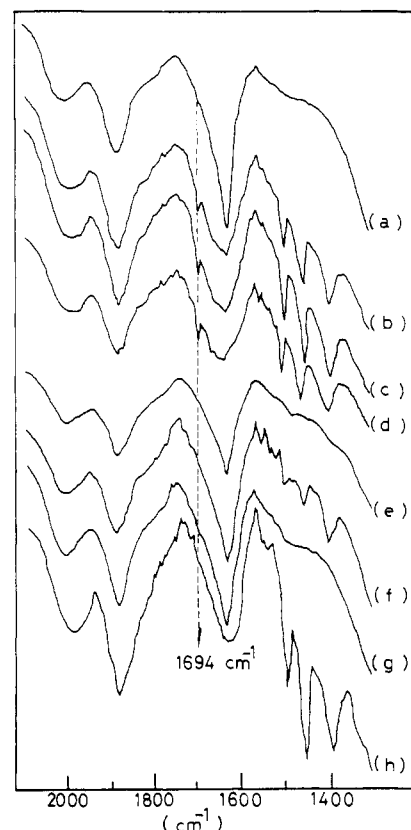


Figure 11. IR spectra of the benzyl alcohol adsorbed on Cu(II)(70)-NaZ and Cu(II)(9)-NaZ: (a) Cu(II)(70)-NaZ calcined at 773 K for 2 h (background); (b) sample a 30 min after benzyl alcohol was adsorbed at room temperature; (c) sample b after 30 min; (d) sample c after 2 h; (e) Cu(II)(9)-NaZ calcined at 773 K for 2 h under O_2 (background); (f) sample e 2 h after benzyl alcohol was adsorbed at room temperature; (g) Cu(II)(70)-NaZ degassed at 773 K for 2 h; (h) sample g 2 h after benzyl alcohol was adsorbed at room temperature.

of CO at room temperature, an absorption peak at 1694 cm^{-1} , which can be identified as the stretching vibration of the carbonyl group in benzaldehyde, then appeared, in addition to an absorption peak at 2137 cm^{-1} due to CO adsorbed on Cu(I) ions (Figure 12b). In contrast to the IR absorption peak of CO adsorbed on Cu(I) ions without adsorbates (Figure 12c), an absorption peak at 2157 cm^{-1} was not clear and only a shoulder at 2157 cm^{-1} appeared (Figure 12b). When CO was adsorbed on the Cu(70)-NaZ catalyst pretreated at 373 K for 1 h under 350 Torr of He, following calcination of Cu(70)-NaZ at 773 K for 2 h, some of the Cu(II) ions were found to reduce to Cu(I) ions as indicated by the appearance of IR absorption bands at 2157 and 2138 cm^{-1} (Figure 12c), though the intensities were relatively small.

Discussion

In benzyl alcohol oxidation over Cu(II)-NaZ, both the yields of benzaldehyde and deep oxidation products ($\text{CO}_2 + \text{CO}$) were found not to decrease with process time, in contrast to the oxidation over Cu(II)-NaY zeolite^{9,11} in which the catalytic activity markedly decreased at the initial time on stream. The difference in the stabilities of oxidation activity with process time between ZSM-5 type and Y type zeolites will be attributed to a difference in the ease of coke deposition in the zeolite pores. Coking of the Y type zeolite has been observed to be much higher than that of the ZSM-5 type zeolite.^{16,17}

The oxidation activity tended to increase with an increase in the extent of ion exchange of Cu(II) ions. The marked increase in both the yields of benzaldehyde and carbon oxides ($\text{CO}_2 + \text{CO}$) at degrees of ion exchange of Cu(II) ion of more than ca.

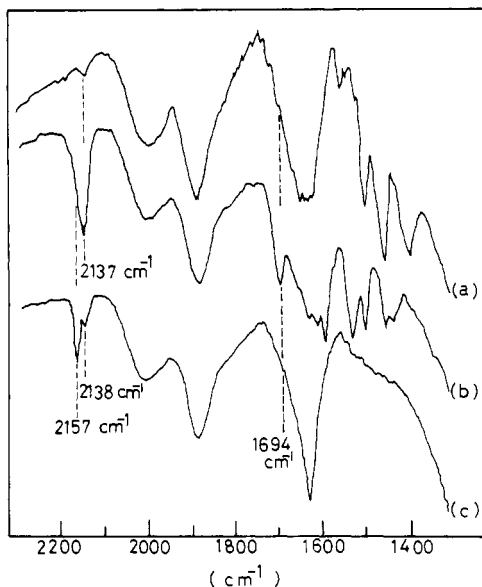


Figure 12. Variation in the IR spectra during the reaction of benzyl alcohol catalyzed by Cu(II)(70)-NaZ: (a) Cu(II)(70)-NaZ degassed at 773 K for 2 h followed by the adsorption of benzyl alcohol at room temperature for 2 h and standing for 1 h under He at 350 Torr; (b) Cu(II)(70)-NaZ treated at 773 K for 2 h under O₂ atmosphere followed by the adsorption of benzyl alcohol at room temperature for 2 h, standing at 373 K for 1 h under He at 350 Torr, and CO (50 Torr) adsorption at room temperature for 5 min (followed by 5 min of degassing at room temperature); (c) Cu(II)(70)-NaZ treated at 773 K for 2 h under O₂ atmosphere followed by standing at 373 K for 1 h under He at 350 Torr and CO (50 Torr) adsorption at room temperature for 5 min (followed by 5 min of degassing at room temperature).

40% (Figure 3) seems to correlate with a sharp increase in the intensity of Cu(I) ions at degrees of Cu(II) ion exchange of more than ca. 40% (Figure 8), though the yield of benzaldehyde tended to inversely decrease with a further increase in the degree of Cu(II) ion exchange. This may imply that the copper species ion-exchanged at higher percent Cu(II) ion exchange have stronger oxidation ability and/or are present under circumstances which cause the substrates to oxidize more easily.

No deep oxidation occurred over the Cu-NaZ catalyst without gaseous oxygen. On the other hand, benzaldehyde formation was observed even after the oxygen supply was removed, as illustrated in Figure 4, though the yield was considerably small. Furthermore, the order of the benzaldehyde yield under a nitrogen atmosphere was found to be identical to the order of the degree of the ion-exchanged Cu ions. From these results, it seems reasonable to assume that, in contrast to deep oxidation products, the oxygen species interacting with copper ions participate in the formation of benzaldehyde.

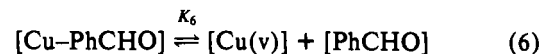
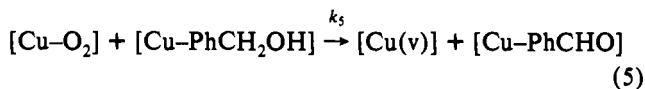
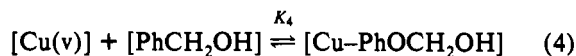
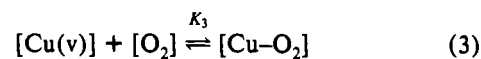
In the IR spectra of benzyl alcohol adsorbed on Cu(II)-NaZ zeolites, Cu(II)(70)-NaZ which has a higher percentage of ion-exchanged Cu(II) ions had a clear absorption peak due to the carbonyl group of benzaldehyde, but the lower ion-exchanged Cu(II)-ZSM-5 zeolite (Cu(II)(9)-NaZ) showed no carbonyl absorption band due to the benzaldehyde product (Figure 11b). These results indicate that higher ion-exchanged Cu(II) ions have higher oxidation activity because of their easier access to reactants and/or their high oxidation ability, in comparison to those of the lower ion-exchanged materials. These results are also consistent with those illustrating the effect of the ion-exchanged Cu(II) ions on the oxidation reaction of benzyl alcohol as mentioned previously.

The Cu(II) ions in a ZSM-5 zeolite were found to be easily reduced to the corresponding Cu(I) ions by an evacuation treatment of the Cu(II)-NaZ zeolite; they began to reduce to Cu(I) ions on evacuation at 313 K. Jacobs and his group have previously reported¹⁹ that the Cu(II) ions in a Y type zeolite

(Cu(II)-NaY zeolite) began to reduce to Cu(I) ions on evacuation at >650 K. The Cu(II) ions in a ZSM-5 zeolite are thereby concluded to be more easily reducible than those in the Y type zeolite.

The Cu(II) ions in a Y type zeolite can be present in both hexagonal prism (SI) and supercage (SII) sites, resulting in the specific relationship between the oxidation activity and the percentage of ion-exchanged Cu(II) ions.^{9,11,23} Some studies on the location of Cu(II) ions in a ZSM-5 zeolite were reported.²³⁻²⁶ The evidence for the presence of more than two kinds of Cu(II) species in a ZSM-5 zeolite has been reported on the basis of TPD spectra of CO adsorbed on Cu(II)-NaZ zeolites and phosphorescence spectra of Cu(I)-NaZ zeolites.²⁴ Kucherov et al. also recently reported²⁷ that the Cu(II) ions in a HZSM-5 zeolite are present in at least two different sites on the basis of ESR spectra of the Cu(II)-HZSM-5 zeolites and semiempirical MO calculations of the model structure of part of the HZSM-5 zeolite. They have also suggested that the sorption of some simple chemical species like *n*-hexane causes a change in Cu(II) ion coordination, which is explained by a slight geometrical displacement, on the basis of ESR spectroscopic evidence.^{26,27} Two IR absorption peaks were observed in this study when CO was adsorbed on Cu-NaZ pretreated by degassing at higher temperature. These data suggest the possibility of at least two classes of Cu species in the NaZSM-5 zeolites. We are now investigating in detail the nature of the Cu species in NaZSM-5 zeolites.

From the kinetic results, one plausible reaction scheme for benzaldehyde formation is as follows:



where Cu(v) is the Cu ion without adsorbed species. The adsorption of molecular oxygen and benzyl alcohol on Cu(v) ions is considered as the first step as shown in eqs 3 and 4, respectively. Equation 5 is the surface reaction between adsorbed oxygen species and an adsorbed benzyl alcohol molecule, which is considered the rate-determining step. The desorption process of benzaldehyde product is shown in eq 6. If it is assumed that K_3 and $K_6 \gg K_4$, the formation rate of benzaldehyde, r_{PhCHO} is expressed as follows:

$$r_{\text{PhCHO}} = k' [\text{PhCH}_2\text{OH}] / [\text{O}_2] \quad (7)$$

where

$$k' = k_5 K_3 [\text{Cu}(v)] / K_4 \quad (8)$$

Equation 7 is in agreement with the rate equation 2, which was obtained experimentally.

From the variation in the IR spectra of benzyl alcohol adsorbed on the Cu(II)(70)-NaZ zeolite which had oxidation activity, under the oxidation/reduction treatments, it was directly observed that Cu(II) ions in NaZSM-5 zeolites oxidize benzyl alcohol to

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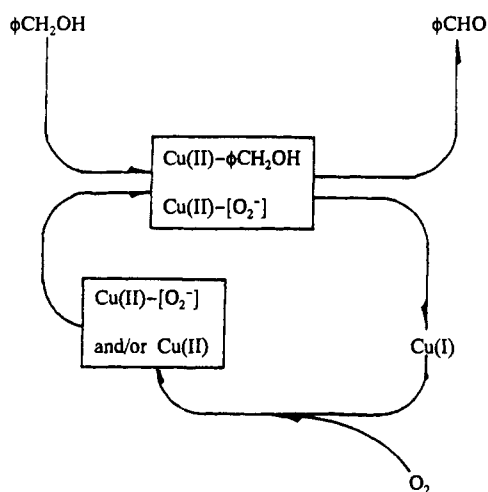
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(26) Kucherov, A. U.; Slinkin, A. A. *J. Phys. Chem.* 1989, 93, 864.

(27) Slinkin, A. A.; Kucherov, A. V.; Chuvylkin, N. D.; Korsunov, V. A.; Kliachko, A. V.; Nikishenko, S. B. *J. Chem. Soc., Faraday Trans. 1* 1989, 85, 3233.

Scheme I



produce benzaldehyde and the Cu(II) ions themselves are simultaneously reduced to Cu(I) ions (Figure 12). The reduced

Cu(I) ions were found to reoxidize to Cu(II) ions in the presence of molecular oxygen (Figure 9).

The overall reaction for benzyl alcohol oxidation to benzaldehyde catalyzed by Cu(II)-NaZ is thus considered to proceed according to Scheme I on the basis of the results of benzyl alcohol oxidation, the reaction kinetics, and the in-situ IR spectra of benzyl alcohol adsorbed on the Cu(II)-NaZ catalyst. Cu(II)-[O₂⁻] species indicate copper-oxygen adducts, though their presence and structures are not experimentally evident at the present stage. Since molecular oxygen thus has the role of reoxidizing Cu(I) ions to the corresponding divalent Cu ions, the oxygen species may have a superoxide form. From the kinetic results showing that the surface reaction between adsorbed benzyl alcohol and oxygen is the rate-determining step as mentioned previously, the Cu(I) to Cu(II) reoxidation step is considered to be a faster reaction step.

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