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The Effect of Alkali Promoters on Cu–Na-ZSM-5 Catalysts in the Oxidation of Benzyl Alcohol

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The oxidation activities of alkali-added Cu–Na-ZSM-5 zeolites in the gas-phase catalytic oxidation of benzyl alcohol were studied. The main products were benzaldehyde and carbon oxides (carbon dioxide + carbon monoxide). The partial oxidation activity was found to markedly increase when an alkali-metal-added Cu–Na-ZSM-5 was used, in comparison with that obtained when the Cu–Na-ZSM-5 zeolite itself was used. On the other hand, the increase in yield of deep oxidation products (CO_2 + CO) catalyzed by the alkali-added Cu–Na-ZSM-5 was rather low. The alkali added to the Cu–Na-ZSM-5 zeolite was thus found to selectively promote catalytic activity for the partial oxidation of benzyl alcohol. Certain types of alkali salts were used as the additive with the results that Na^+, K^+, and Rb^+, but not Li^+, had similar behavior for benzyl alcohol oxidation. An alkali oxide such as Na_2O, rather than the alkali salt itself, was suggested to substantially function as an active promoter for the oxidation of benzyl alcohol as judged from the pretreatment condition of the alkali-added Cu–Na-ZSM-5 zeolite and its similar catalytic activity in the oxidation of alkali salts with the same alkali cation but different counteranions. The added alkali was found to act more effectively as a promoter for oxidation when alkali and Cu ions were accessible to each other; therefore the alkali was suggested to interact directly with the Cu ion to promote the oxidation of benzyl alcohol, rather than this promotion being a separate function of the alkali itself. One of the roles of the alkali added to the Cu–Na-ZSM-5 zeolite was promoting the dissociation of the oxygen molecule, as evidenced by the results of the exchange reaction of the oxygen molecule. The alkali was also suggested to neutralize the acid sites in the Cu–Na-ZSM-5 zeolite and prevent its deactivation by retarding the formation of coke-like materials on the zeolite. © 1995 Academic Press, Inc.

INTRODUCTION

Copper(II) ions ion-exchanged in a zeolite have been reported to have a redox function and have been used as catalysts for various gas-phase catalytic oxidations (1–10). In the gas-phase oxidation of an organic compound, it is usually difficult to control the selectivity of a partial and/or deep oxidation, which has been regulated mainly through the reaction temperature. However, lower temperature tends to cause a decrease in the oxidation activity, though the selectivity of a partial oxidation product generally increases. We have previously reported (11–13) the catalysis of a basic copper(II) catalytic system (Cu(II) salt + inorganic base) in the liquid-phase oxidation of phenol derivatives, in which inorganic bases, such as KOH, has been found to be effective in the oxidation of phenols. Only copper(II) chloride had no oxidation activity, but the corresponding basic copper(II) system (copper(II) chloride + KOH) showed considerable oxidation activity for the phenol derivatives (11–13). More recently the influence of alkali-modified zeolites on basic catalytic activity has been reported by Davis and his coworkers (14–16).

Armed with this knowledge, we have tried to use the Cu ion-exchanged ZSM-5 zeolite, which was treated with an alkali, such as NaOH, as a catalyst for the gas-phase oxidation of benzyl alcohol, as reported in our preliminary report (17). In this work, an alkali-added Cu–Na-ZSM-5 zeolite is studied as a catalyst for the gas-phase catalytic oxidation of benzyl alcohol. An alkali, such as NaOH, added to the Cu–Na-ZSM-5 was found to be a very effective additive for the oxidation of benzyl alcohol, particularly for partial oxidation. The alkali-added Cu–Na-ZSM-5 caused a higher yield of the partial oxidation product and a low level of deep oxidation products at the higher reaction temperature, in contrast to the previously described oxidation over non-alkali-added zeolites. The effect of the added alkali on the degree of ion-exchange of the Cu ions was investigated in connection with the yield of both partial and deep oxidation products.

EXPERIMENTAL

Catalysts

A Na-ZSM-5 zeolite was prepared using the method described in a patent (18). The prepared zeolite, which was washed with boiled deionized water for 2 h and dried overnight at room temperature, was further treated with

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an aqueous solution of sodium nitrate at 343–345 K for 1 h. This treatment was carried out twice. The $NaNO_3$-treated zeolite was dried at room temperature and at 393 K overnight, and then calcined at 773 K for 5 h. The degree of ion exchange of sodium ion in the ZSM-5 zeolite was found by atomic absorption measurement (Shimazu type AA-630-01) to be 100%. The Cu–Na-ZSM-5 zeolite was prepared by a conventional ion-exchange method, in which the Na–ZSM-5 was treated in an aqueous solution of copper(II) acetate (Nacalai Tesque, guaranteed reagent) at 358 K for 2 h and washed with deionized water, filtered, dried, and calcined at 773 K for 3 h in air. The Si/Al atomic ratio of the Na-ZSM-5 zeolite and the degree of ion exchange of the copper(II) ion in the Cu–Na-ZSM-5 were determined using an atomic absorption spectrometer (Shimazu type AA-630-01) after the Na-ZSM-5 and the Cu–Na-ZSM-5 were homogeneously dissolved by adding two to three drops of hydrogen fluoride solution (Hashimoto Chemicals, guaranteed reagent, 47%) to each. The Si/Al atomic ratio of the Na-ZSM-5 was found to be 35. Two different methods were tried for the preparation of an alkali-added Cu–Na-ZSM-5 zeolite: adsorption and impregnation. In the former method, the Cu–Na-ZSM-5 zeolite was added to an aqueous solution of an alkali, such as NaOH, and the resultant heterogeneous system was allowed to stand at room temperature for ca.1 h during which time the whole system was vigorously stirred every 10 min, then filtered, dried, and calcined at 773 K for 3 h in air. An alkali, such as NaOH, in the alkali-adsorbed Cu–Na-ZSM-5 ($alkali_{ads}$–Cu–Na-ZSM-5) was quantitatively analyzed by volumetrically measuring the difference in the alkali concentrations before and after the adsorption of the alkali on the Cu–Na-ZSM-5 zeolite. A 1-cm^3 aliquot (1–2 drops BTB indicator added) of the alkali solution was titrated with HCl standard solution. The alkali-impregnated Cu–Na-ZSM-5 ($alkali_{imp}$–Cu–Na-ZSM-5) was prepared by the impregnation method. As described under Results, the alkali-added Cu–Na-ZSM-5 zeolites prepared by the two different methods were found to have almost similar catalytic behavior. The XRD pattern of the Na-ZSM-5 synthesized showed a pattern typical of Na-ZSM-5 zeolite peaks. From the observation of the XRD patterns, both the Cu–Na-ZSM-5 and alkali-added Cu–Na-ZSM-5 zeolites were confirmed not to destroy the zeolite structure.

Gas-Phase Catalytic Oxidation of Benzyl Alcohol

The gas-phase catalytic oxidation of benzyl alcohol was performed at atmospheric pressure using a conventional fixed-bed continuous-flow microreactor, which was made from a Pyrex glass tube with inner diameter 15 mm. Benzyl alcohol was continuously supplied to the reactor through a microfeeder. The thermocouple was located in the middle of the catalyst bed. Prior to the reaction, the catalyst was calcined at 773 K for 2 h in a mixed flow of oxygen and nitrogen (mole ratio, 1 : 4). The standard reaction conditions were as follows: catalyst amount (W), 0.5 g; partial pressure of oxygen (P_{O_2}), 8.75×10^3 Pa; partial pressure of benzyl alcohol (P_B°), 2.59×10^3 Pa; W/F(F = total mole flow rate), 3.61×10^{-1} g-cat · h/mol. The liquid-phase products and unreacted reagent were trapped at 251 K (the refrigerant consisted of tetrachlorocarbon and liquid nitrogen) and analyzed by gas chromatography with an FID detector (Shimazu type GC-3A), using a 10% silicon OV-17 on chromosorb GAW DMCS (3 m) at 473 K under a nitrogen carrier (30 cm^3/min) after the mixed reaction solution was diluted with isopropanol as an internal standard. The gaseous products were collected in a 1-cm^3 gas sampler connected directly to the reactor and analyzed using a Shimazu GC-6A type chromatograph (equipped with a TCD detector) which was also directly connected to the flow microreactor, using the intermediate cell method (19) with a 1-m column packed with silica gel at 393 K and a 3-m column of 5A molecular sieves at 293 K using a hydrogen carrier (35 cm^3/min). The carbon balances before and after the catalytic oxidation were found to be usually more than 90%. The conversion of benzyl alcohol and the yields of benzaldehyde and CO_2 + CO were defined as follows:

Conversion (%) = {([moles of benzaldehyde produced] + $\frac{1}{7}$ × [moles of CO_2 + CO produced])/[moles of benzyl alcohol fed]} × 100;

Yield of benzaldehyde (%) = {[moles of benzaldehyde produced]/[moles of benzyl alcohol fed]} × 100; and

Yield of (CO_2 + CO) (%) = {$\frac{1}{7}$ × [moles of CO_2 + CO produced]/[moles of benzyl alcohol fed]} × 100.

Measurements of NH_3 and CO_2 Adsorbed Amounts

The measurements of the adsorbed amounts of NH_3 and CO_2 gases on the zeolites were performed using conventional low-pressure static-type gas adsorption equipment. Its vacuum line consisted of an adsorption chamber containing the zeolite sample (0.05 g) and a manometer. Before introduction of the adsorption gas, the zeolite sample was calcined at 773 K for 1 h under 150 Torr oxygen and degassed at 773 K for 1 h. After the measurement of the dead volume, 100 Torr of adsorption gas (NH_3 or CO_2) was introduced into the adsorption system. The total adsorbed amount was measured after 1 h at which time the adsorption equilibrium was confirmed. After evacuating the zeolite sample for 1 h at room temperature, the previously described adsorption treatment was again repeated and the reversible adsorption amount was measured. An irreversible adsorption amount was here defined as the difference between the total and reversible adsorption amounts.

Measurement of CO Adsorbed Amount

The adsorption of CO was carried out using a semimicro, low-pressure, static-type, gas adsorption apparatus which consisted of a capillary glass tube to make the dead volume as small as possible. The zeolite sample was pretreated at 773 K for 1 h under an oxygen atmosphere of 150 Torr followed by evacuation at 773 K for 2 h. A similar operation for the NH_3 and CO_2 adsorption was conducted except for the introduction of CO at 20 Torr. The total, reversible, and irreversible adsorption amounts were obtained as described previously.

$^{18}O_2$–$^{16}O_2$ Exchange Reaction

The $^{18}O_2$–$^{16}O_2$ exchange reaction was carried out using low-pressure closed circular reaction equipment. The catalyst (0.05 g) in the reaction chamber was calcined at 773 K for 1 h under an oxygen atmosphere of 150 Torr and evacuated at 773 K for 2 h before the exchange reaction. The exchange reaction was started after the introduction of an equimolar mixture of $^{18}O_2$ and $^{16}O_2$ at 40 Torr (20 Torr each). The reaction gas was sampled at each time interval and analyzed by a mass spectrometer (Hitachi Model RM-60).

IR Spectra of the Adsorbed CO on the Zeolite Catalysts

The IR spectra of the adsorbed CO on the zeolite catalysts were observed at room temperature using an Analect Model FX-6200 FTIR spectrophotometer with a highly sensitive HgCdTe detector. The zeolite powder (ca. 20 mg), sieved to less than 100 mesh, was compressed (400 kg/cm^2, 10 min) to a wafer (inner diameter, 20 mm), which was self-supported in an *in situ* cell. The wafer in the *in situ* cell was calcined at 773 K for 1 h in an oxygen atmosphere of 150 Torr followed by evacuation at 773 K for 2 h. The IR spectra of the adsorbed CO were measured by introducing 50 Torr of CO into the *in situ* cell.

RESULTS

Oxidation Activity of Alkali-Added Cu–Na-ZSM-5 Zeolites in Benzyl Alcohol Oxidation

The main oxidation products were deep oxidation products, CO_2 + CO (CO_2/CO ≈ 10), and a partial oxidation product, benzaldehyde, regardless of the presence of an alkali, such as NaOH, in the Cu-Na-ZSM-5. Under certain reaction conditions, traces of benzene and/or toluene were formed as minor products for these two Cu–Na-ZSM-5 catalytic systems with and without alkali.

Table 1 shows the effect of alkali addition in both the Cu–Na-ZSM-5 and the Na-ZSM-5 zeolites on product yields. The formation rates of benzaldehyde ($r_{\mathrm{Benzaldehyde}}$) and CO_2 + CO (r_{CO_2+CO}) were also calculated based on the principle of a different reactor. Yields of both benzaldehyde and CO_2 + CO from the NaOH impregnated Na-ZSM-5 (NaOH$_{\mathrm{imp}}$–Na-ZSM-5) remained unchanged, with yields almost similar to those from the Na-ZSM-5 zeolite itself. In contrast to the Na-ZSM-5, the NaOH-impregnated Cu-Na-ZSM-5 (NaOH$_{\mathrm{imp}}$-Cu-Na-ZSM-5) had a very high yield for benzaldehyde and a slightly higher yield of CO_2 + CO in comparison with the Cu–Na-ZSM-5 zeolite. From these results, it is evident that the added alkali alone, such as NaOH, had no effect on benzyl alcohol oxidation activity; instead, the presence of both the Cu ion and the alkali abruptly caused a high yield of the partial oxidation product, benzaldehyde.

The relationship between conversion and time on stream for benzyl alcohol oxidation catalyzed by Cu(67)–Na-ZSM-5 (percent of Cu ion-exchange, 67%) and NaOH$_{\mathrm{imp}}$–(6.35)–Cu(67)–Na-ZSM-5 (added Na/Cu atomic ratio, 6.35) zeolites is illustrated in Fig. 1. It is evident that alkali addition to the Cu–Na-ZSM-5 zeolite caused a marked increase in conversion. The high conversion was maintained almost unchanged in the investigated range for the time on stream. The results for the used NaOH$_{\mathrm{imp}}$(6.35)–Cu(67)–Na-ZSM-5, which was calcined at 773 K for 5 h in air after use as a catalyst for benzyl alcohol oxidation, are also shown in Fig. 1 for comparison. The conversion over the used alkali-added Cu–Na-ZSM-5 was found to be almost identical to that over the corresponding fresh zeolite; no deactivation of the used zeolite catalyst was seen. The high oxidation activity of the alkali-added Cu–Na-ZSM-5 thus remained almost unchanged even for the corresponding used zeolite. It is of interest to note that when we observed the used Cu–Na-ZSM-5 zeolite after the oxidation reaction with the naked

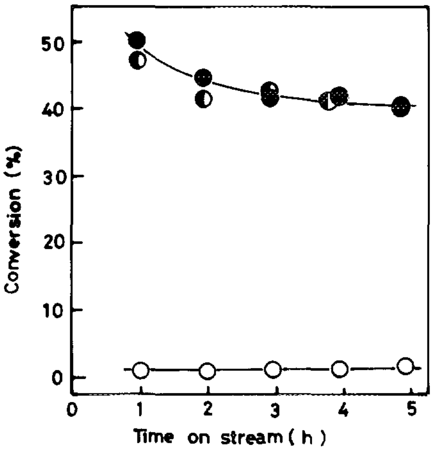

FIG. 1. The relationship between the conversions in benzyl alcohol oxidation over Cu–Na-ZSM-5 and alkali added Cu–Na-ZSM-5 zeolites vs time on stream. Reaction temperature, 673 K; ○, Cu(67)–Na-ZSM-5; ●, NaOH$_{\mathrm{imp}}$–Cu(67)–Na-ZSM-5 (added Na/Cu = 6.35); ◐, Used NaOH$_{\mathrm{imp}}$–Cu(67)–Na-ZSM-5 (Na/Cu = 6.35) calcined at 773 K for 5 h.

TABLE 1

Effect of NaOH Addition on the Oxidation of Benzyl Alcohol[a]

Catalyst	NaOH amount (mol/g cat)	Yield (%)		Rate (r) (mol/h^{-1} · g cat)	
		Benzaldehyde	CO_2 + CO	$r_{benzaldehyde}$	r_{CO_2+CO}
Na-ZSM-5	0	1.7	0.1	4.7×10^{-2}	2.8×10^{-3}
$NaOH_{imp}$–Na-ZSM-5	9.6×10^{-4}	1.2	0.1	3.3×10^{-2}	2.8×10^{-3}
Cu(54)–Na-ZSM-5	0	3.5	7.5	9.7×10^{-2}	2.1×10^{-1}
$NaOH_{imp}$–Cu(54)–Na-ZSM-5	9.6×10^{-4}	70.7	11.8	1.96	3.3×10^{-1}

[a] Reaction temperature, 673 K.

eye, its surface appeared black because of the accumulation of a coke-like material which caused a deactivation of the oxidation reaction, but the surface of the used NaOH-added Cu–Na-ZSM-5 zeolite remained almost unchanged after oxidation and carbonaceous material was not observed. Although we did not study the effect of the added alkali on the deactivation of the oxidation reaction in detail, at the present stage, the alkali added in the Cu–Na-ZSM-5 inhibits the accumulation of the undesirable carbonaceous material on the zeolite surface.

The effect of the reaction temperature on the oxidation activities of both the Cu–Na-ZSM-5 and the $NaOH_{ads}$–Cu–Na-ZSM-5 catalysts was studied in detail using varied amounts of added alkali and the degree of ion-exchange of Cu ion in these zeolites, with the results shown in Table 2. It is evident that the conversion increased with increased reaction temperature regardless of the presence of NaOH in the Cu–Na-ZSM-5 zeolite. The $NaOH_{ads}$–Cu–Na-ZSM-5 zeolites were found to have higher conversions than the Cu–Na-ZSM-5 zeolites themselves over all the ranges of the reaction temperature studied here. The increase in conversion with respect to reaction temperature is significant in the $NaOH_{ads}$–Cu–Na-ZSM-5 systems in which the amount of added alkali was relatively high. Focusing on the product yields, it is of interest to note that most of the increases in the conversion are due to the increase in benzaldehyde yield. The yields of carbon oxides (CO_2 + CO, the deep oxidation products), over the NaOH-added Cu–Na-ZSM-5 zeolites increased only slightly even in the high temperature region. The alkali added to the Cu–Na-ZSM-5 was thus found to selectively promote partial oxidation activity.

A comparison of the oxidation activities of the alkali-added Cu–Na-ZSM-5 catalysts prepared by both impregnation and adsorption methods is shown in Table 3. From these results it seems reasonable to consider that no substantial difference in either of the oxidation activities is present.

The effect on oxidation activity of the amount of the NaOH added to the Cu–Na-ZSM-5 was studied for a constant amount of Cu ion using NaOH-added Cu–Na-ZSM-5 zeolites prepared by impregnation methods ($NaOH_{imp}$–Cu(54)–Na-ZSM-5); the results are shown in

TABLE 2

Effect of Reaction Temperature on the Oxidation Activity over $NaOH_{ads}$–Cu–Na-ZSM-5 Catalyst

Percentage of Cu ion-exchanged (%)	Reaction temperature (T)	Added Na/Cu (atomic ratio)	Yield (%)	
			Benzaldehyde	CO_2 + CO
9	673	0	4.8	0.5
		1.2	8.3	0.5
		2.6	16.5	1.0
69	573	0	1.7	0.1
		1.7	3.8	0.5
		3.4	5.0	1.0
	623	0	4.3	0.1
		1.7	6.5	0.3
		3.4	11.5	1.0
	673	0	5.7	0.3
		1.7	16.4	0.6
		3.4	48.5	1.5

TABLE 3

Effect of Preparation Method of Alkali Added Cu(67)–Na-ZSM-5 on the Oxidation Activity[a]

Preparation method	Added Na/Cu (atomic ratio)	Conversion (%)	Yield (%)	
			Benzaldehyde	CO_2 + CO
No alkali treatment	0	13.6	2.6	10.3
Adsorption method	5.4	81.1	66.1	13.1
Impregnation method	5.4	84.4	71.1	12.1

[a] Reaction temperature, 673 K.

Fig. 2. The yield of benzaldehyde increased with an increase in the amount of added NaOH. Particularly, the yield of the partial oxidation product, benzaldehyde, abruptly increased with an increase in NaOH in the range of the lower atomic ratios of added Na/Cu. The increase in the yield of the deep oxidation products with the amount of NaOH was not as high as in the partial oxidation. The role of the alkali was thus, once again, confirmed to be the selective activation of the partial oxidation. The influence on the product yields of the excess amount of NaOH for a constant amount of Cu ion is also illustrated in Fig. 2. The added Na/Cu atomic ratios of more than ca. 8 inversely caused a decrease in the yields. Too high an amount of NaOH on the Cu ion was thus found to inhibit partial oxidation. The variation in the yield of deep oxidation products, CO_2 + CO, with the added Na/Cu atomic ratio showed a behavior similar to that of the benzaldehyde yield though the degree of the increase in the yield of CO_2 + CO was much lower.

Figure 3 illustrates the effect of the percentage of the ion-exchange of Cu ion on the yields of the oxidation products at the constant added Na/Cu atomic ratio of 5.4. The yield of benzaldehyde increased with increasing percentage of ion-exchanged Cu ions up to nearly 80% ion-exchanged Cu, but beyond ca. 80% ion-exchanged Cu, the yield of benzaledhyde inversely decreased. Similar behavior has been already observed (21) in the relationship between the benzaldehyde yield and the percentage of ion exchange of Cu ions in benzyl alcohol oxidation catalyzed by the Cu–Na-ZSM-5 zeolite without added alkali.

To investigate the role of oxygen, after the supply of oxygen was stopped in the course of the oxidation of benzyl alcohol oxidation on $NaOH_{imp}$–Cu(65)–Na-ZSM-5 catalyst, the yield of each oxidation product was followed as a function of time on stream, as shown in Fig. 4. No deep oxidation products were observed in the oxygen-free atmosphere, regardless of the presence of NaOH. In contrast to the deep oxidation products, benzaldehyde continued to be produced even in an oxygen-free atmosphere (a nitrogen atmosphere), though the yields of benzaldehyde were considerably lower. The yield of benzaldehyde catalyzed by $NaOH_{imp}$–Cu–Na-ZSM-5 in an oxygen-free atmosphere was appreciably higher than that catalyzed by Cu–Na-ZSM-5 zeolite under the same reaction conditions. From these results, it is considered that the gas-phase oxygen molecule is necessary in order to

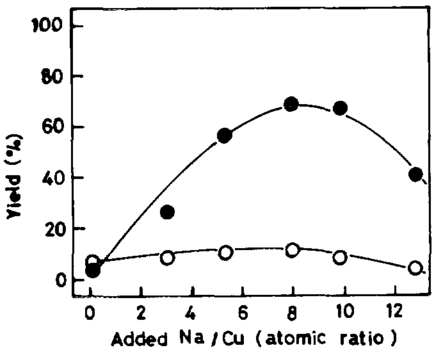

FIG. 2. The effect of added Na/Cu atomic ratio on the yields in the benzyl alcohol oxidation over $NaOH_{imp}$–Cu(54)–Na-ZSM-5 zeolite. Reaction temperature, 673 K; ●, benzaldehyde; ○, CO_2 + CO.

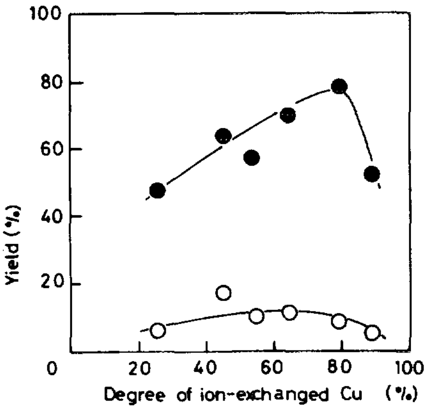

FIG. 3. The effect of degree of the ion-exchanged Cu in $NaOH_{imp}$–Cu–Na-ZSM-5 zeolite on the yields in the benzyl alcohol oxidation. Reaction temperature, 673 K; added Na/Cu atomic ratio, 5.4; ●, benzaldehyde; ○, CO_2 + CO.

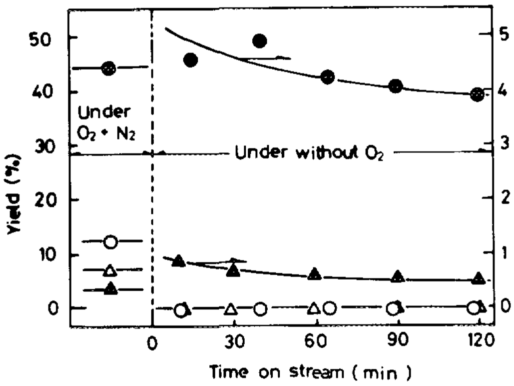

FIG. 4. The effect of gaseous oxygen molecule on the benzyl alcohol oxidation over Cu–Na-ZSM-5 and $NaOH_{imp}$–Cu(54)–Na-ZSM-5 zeolites. Reaction temperature, 673 K; ○, △, Cu(67)–Na-ZSM-5; ●, ▲, $NaOH_{imp}$–Cu(67)–Na-ZSM-5 (added Na/Cu = 3.4); ●, ○, benzaldehyde; ▲, △, CO_2 + CO.

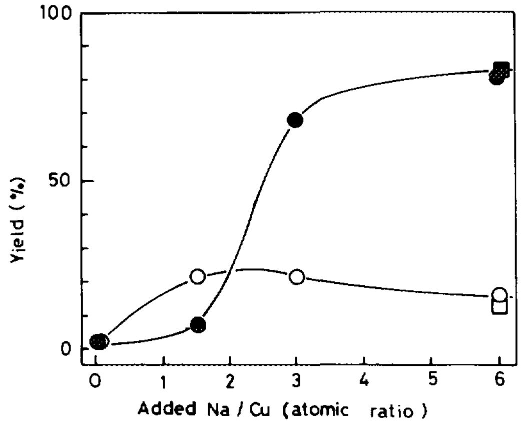

FIG. 5. The effect of added Na/Cu atomic ratio on the yields in the benzyl alcohol oxidation over alkali added Cu–Na-ZSM-5 zeolites. Reaction temperature, 673 K; ●, ○, $NaNO_{3imp}$–Cu(65)–Na-ZSM-5; ■, □, CH_3COONa_{imp}–Cu(65)–Na-ZSM-5; ●, ■, benzaldehyde; ○, □, CO_2 + CO.

yield deep oxidation products, and the formation of the partial oxidation product is connected with the adsorbed oxygen species and/or the homologues.

It is of interest to investigate the influence on oxidation activity of the spatial access between the added alkali and the Cu ions from the point of view of studying the role of the alkali added to the Cu–Na-ZSM-5 zeolite. Table 4 shows the oxidation activity of a catalytic system in which Cu–Na-ZSM-5 and a NaOH-impregnated Na-ZSM-5 zeolite ($NaOH_{imp}$–Na-ZSM-5) were physically mixed, together with the catalytic activity of NaOH-impregnated Na-ZSM-5 zeolite ($NaOH_{imp}$–Na-ZSM-5). The mixed catalytic system of the Na-ZSM-5 and the NaOH-impregnated Na-ZSM-5 had only low activities for both deep and partial oxidation. The yield of the partial oxidation product, benzaldehyde, was found to increase appreciably for the physically mixed catalytic system of the Cu–Na-ZSM-5 and the $NaOH_{imp}$–Na-ZSM-5. However, it is evident from Table 4 that the physically mixed catalytic system has lower catalytic activity for benzyl alcohol oxidation than the $NaOH_{imp}$–Cu–Na-ZSM-5 catalyst. The yields of both deep oxidation products for these two catalytic systems were not very different from each other. These results imply that the direct concerted interaction between Cu ions and the added alkali, rather than the separated independent function of both the Cu ions and the added alkali, is an important factor promoting partial oxidation.

As an additive for Cu–Na-ZSM-5, we tried to use some salts including the Na^+ cation, in addition to NaOH. Figure 5 illustrates the effects of the impregnated $NaNO_3$ and CH_3COONa on the yields of benzyl alcohol oxidation. These two additives were also found to promote oxidation activity, just like the previously described NaOH additive. The yield of benzaldehyde sharply increased at added Na/Cu atomic ratios of more than ca. 1.5. On the other hand, the degree of increase in the deep oxidation yield was not as high as the increase in the added Na/Cu atomic ratios. Similar behavior was also observed using a CH_3COONa additive (added Na/Cu atomic ratio, 6). From the results of Fig. 5 and the fact that the sodium

TABLE 4

Effect of the Mixed Method of the Added Alkali and Cu(65)–Na-ZSM-5 Zeolite on the Oxidation Activity[a]

Catalytic system[b]	Yield (%) Benzaldehyde	Yield (%) CO_2 + CO
Na-ZSM-5 + Cu(65)–Na-ZSM-5	3.7	2.0
$NaOH_{imp}$–NaZSM-5 + Cu(65)–Na-ZSM-5	17.4	7.7
Na-ZSM-5 + $NaOH_{imp}$–Cu(65)–Na-ZSM-5	48.8	7.9

[a] Reaction temperature, 673 K; amount of added NaOH, 9.6×10^{-4} mol/g cat.
[b] 0.25 g of each was mixed.

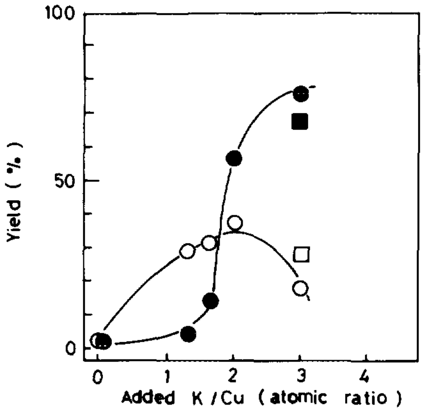

FIG. 6. The effect of added K/Cu atomic ratio on the yields in the benzyl alcohol oxidation over alkali added Cu–Na-ZSM-5 zeolite. Reaction temperature, 673 K; ●, ○, KOH_{imp}–Cu(65)–Na-ZSM-5; ■, □, $KNO_{3_{imp}}$Cu(65)–Na-ZSM-5; ●, ■, benzaldehyde; ○, □, CO_2 + CO.

salt-impregnated Cu–Na-ZSM-5 zeolites were calcined at 773 K for 2 h in air, it seems reasonable to consider that these additives would be converted to the corresponding oxide form, such as the Na_2O species, as in the case of the NaOH additive.

To study the effect of the alkali metal ion on the oxidation activity, KOH, KNO_3, RbOH, and LiOH were used as additives for the Cu–Na-ZSM-5 zeolite, as illustrated in Figs. 6–8. The behavior of KOH, KNO_3, and RbOH additives in benzyl alcohol oxidation were similar to that of the NaOH additive; thus the yield of benzaldehyde significantly increased with added K/Cu or added Rb/Cu atomic ratios, and the deep oxidation was moderately promoted by adding these additives to the Cu–Na-ZSM-5 zeolites. On the other hand, the effect of LiOH additives on oxidation activity seems fairly different from that of other alkali hydroxides. Although the addition of LiOH causes an increase in oxidation activity, the degree of increase in the benzaldehyde yield was not as high as the case of the addition of NaOH, and in contrast, the yield of deep oxidation products tended to become higher than that of partial oxidation products. In contrast to the other alkali metal ions, the Li^+ cation was found to have a fairly different function for the benzyl alcohol oxidation.

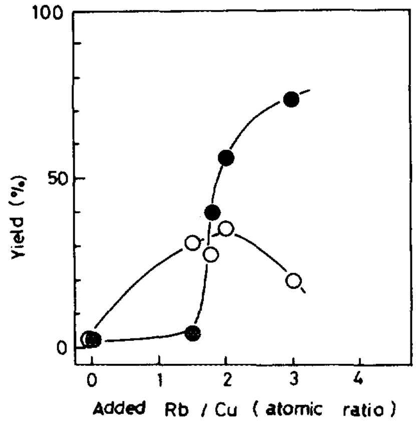

FIG. 7. The effect of added Rb/Cu atomic ratio on the yields in the benzyl alcohol oxidation over $RbOH_{imp}$–Cu–Na-ZSM-5 zeolite. Reaction temperature, 673 K; ●, benzaldehyde; ○, CO_2 + CO.

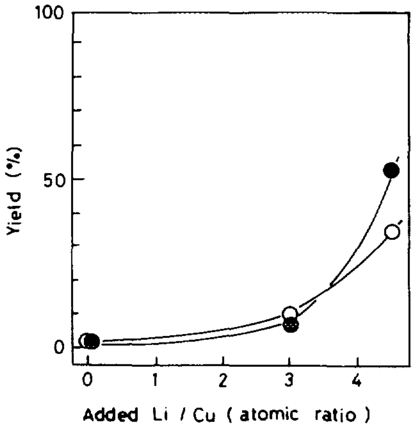

FIG. 8. The effect of added Li/Cu atomic ratio on the yields in the benzyl alcohol oxidation over $LiOH_{imp}$–Cu–Na-ZSM-5 zeolite. Reaction temperature, 673 K; ●, benzaldehyde; ○, CO_2 + CO.

Acidity and Basicity of the Alkali Added Cu–Na-ZSM-5 Zeolites

The amounts of NH_3 and CO_2 adsorbed on both NaOH- and $NaNO_3$-added Cu–Na-ZSM-5 zeolites were measured in order to evaluate the acidity and basicity in these zeolites. The irreversibly adsorbed amounts of NH_3 and CO_2 were taken as measures of the acidity and basicity of the zeolite, respectively. Figure 9 illustrates the variation in the adsorbed amounts of NH_3 on the added Na/Cu atomic

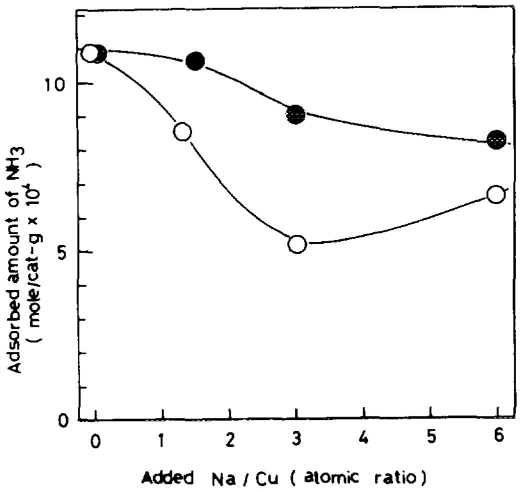

FIG. 9. The adsorption of NH_3 on the alkali added Cu(65)–Na-ZSM-5 zeolites. ●, $NaOH_{imp}$–Cu(65)–Na-ZSM-5; ○, $NaNO_{3_{imp}}$–Cu(65)–Na-ZSM-5; these two zeolites were pretreated at 773 K for 1 h under 150 Torr O_2 followed by evacuation at 773 K for 2 h.

ratios in the alkali-added Cu–Na-ZSM-5 zeolites. The acidity of the alkali-added Cu–Na-ZSM-5 zeolite tended to decrease with an increase in the added Na/Cu atomic ratios. The addition of NaOH caused a greater decrease in acidity than $NaNO_3$ addition. The variation in the basicity of the zeolites on the added Na/Cu atomic ratios is shown in Fig. 10. The basicity tended to increase with increasing atomic ratios of the added Na/Cu, though the increasing basicities of NaOH- and $NaNO_3$-added Cu–Na-ZSM-5 zeolites were appreciably different from each other. The almost linear increase in the benzaldehyde yield catalyzed by $NaOH_{imp}$–Cu–Na-ZSM-5 up to Na/Cu ratios of around 6 (Fig. 2. ●) was similar to the increase in the basicity caused by adding NaOH (Fig. 10, ●); on the other hand, the dependence of benzaldehyde yield catalyzed by $NaNO_{3imp}$–Cu–Na-ZSM-5 on the added Na/Cu ratio showed an S-type shape (Fig. 5, ●), the behavior of which was similar to that of the basicity by adding $NaNO_3$ (Fig. 10, ○).

IR Spectra and Adsorbed Amounts of CO Adsorbed on the $NaOH_{imp}$–Cu–Na-ZSM-5 Zeolites

The IR spectra of CO adsorbed on both the Cu–Na-ZSM-5 and $NaOH_{imp}$–Cu–Na-ZSM-5 zeolites are illustrated in Fig. 11. Two absorption peaks were observed at 2157 and 2135 cm^{-1} when CO was adsorbed on the Cu–Na-ZSM-5 zeolite which was preevacuated at 773 K for 2 h. However, the absorption peak at 2157 cm^{-1} significantly decreased, to be observed only as a shoulder peak, and, in contrast to the peak at 2157 cm^{-1}, the relative intensity of the peak at 2135 cm^{-1} increased when CO was adsorbed on the NaOH-added Cu–Na-ZSM-5 zeolite pretreated at 773 K for 2 h under vacuum.

The amounts of CO adsorbed on the NaOH-added Cu–Na-ZSM-5 zeolite were measured vs the variation in the added Na/Cu atomic ratios. The increase in the added Na/Cu caused a decrease in the adsorbed amounts of CO, as shown in Table 5. The decrease in CO adsorption was also observed when $NaNO_3$ was used as an additive in the Cu–Na-ZSM-5 zeolite.

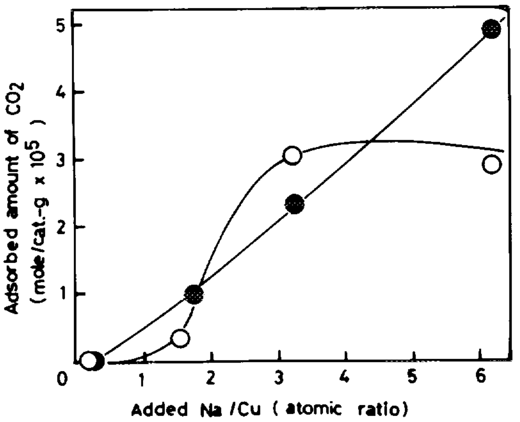

FIG. 10. The adsorption of CO_2 on the alkali added Cu(65)–Na-ZSM-5 zeolites. ●, $NaOH_{imp}$–Cu(65)–Na-ZSM-5; ○, $NaNO_{3imp}$–Cu(65)–Na-ZSM-5; these two zeolites were pretreated at 773 K for 1 h under 150 Torr O_2 followed by evacuation at 773 K for 2 h.

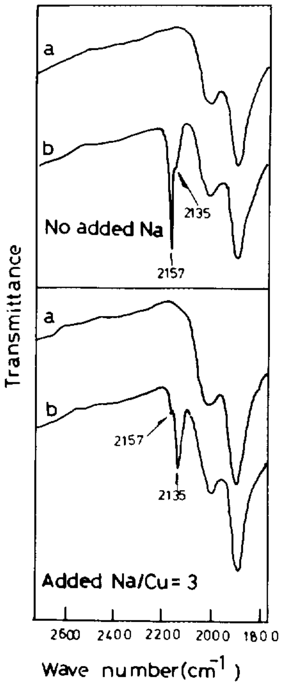

FIG. 11. The IR spectra of CO adsorbed on the Cu(65)–Na-ZSM-5 and Na added Cu(65)–Na-ZSM-5 zeolites. All spectra were measured at room temperature; (a) pretreated at 773 K for 1 h under 150 Torr O_2, followed by the evacuation at 773 K for 2 h; (b) after 50 Torr of CO was adsorbed at room temperature for 5 min and evacuated for 5 min.

Oxygen Molecule Exchange Reaction Catalyzed by $NaOH_{imp}$–Cu–Na-ZSM-5 Zeolite

The $^{18}O_2$–$^{16}O_2$ exchange reaction at 773 K took place in a closed circulation reaction system using Cu–Na-ZSM-5 catalysts both with and without the NaOH additive in

TABLE 5

Amount of CO on an Additive Added Cu(65)–Na-ZSM-5 Zeolite[a]

Additive	Added Na/Cu (atomic ratio)	Adsorbed Amount of CO (mol/g cat × 10^5)
None	0	1.5
NaOH	1.3	0.45
	2.1	0.31
	3.0	0.31
$NaNO_3$	3.0	0.40

[a] The zeolites were evacuated at less than 1.0 × 10^{-4} Torr for 2 h at 773 K before the CO adsorption at room temperature.

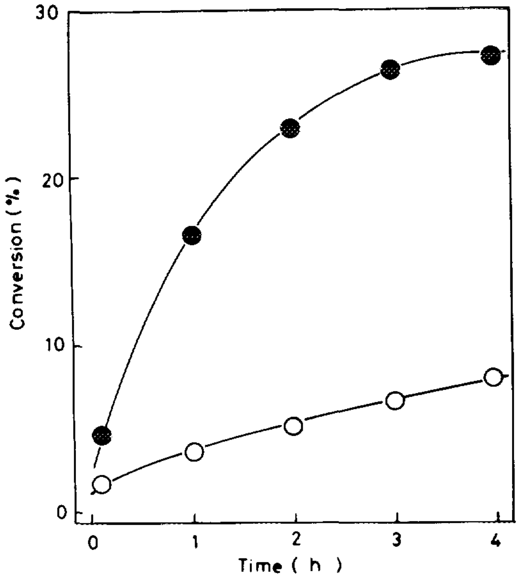

FIG. 12. The $^{18}O_2$–$^{16}O_2$ exchange reaction catalyzed by Cu(65)–Na-ZSM-5 and $NaOH_{imp}$–Cu–Na-ZSM-5 zeolites. Reaction temperature, 773 K; ○, Cu(65)–Na-ZSM-5; ●, $NaOH_{imp}$–Cu(65)–Na-ZSM-5 (added Na/Cu atomic ratio = 3).

order to compare their activities for oxygen molecules. Figure 12 shows the variation in the conversion vs reaction time. It is clear from Fig. 12 that the $NaOH_{imp}$–Cu–Na-ZSM-5 (added Na/Cu atomic ratio, 3) leads to larger catalytic activity for the exchange reaction of oxygen molecules as compared to the corresponding catalyst without NaOH. The alkali added to the Cu–Na-ZSM-5 zeolite is suggested to contribute to the activation of the oxygen molecule through its dissociation.

DISCUSSION

From the results of the oxidation of benzyl alcohol catalyzed by additive-added Cu–Na-ZSM-5 zeolites, the addition of NaOH or KOH was found to promote oxidation activity, particularly partial oxidation activity. Interestingly, it was also observed that $NaNO_3$ and/or CH_3COONa were useful as promoters for oxidation activity. This suggests that the anion parts such as OH^- and NO_3^- are not directly related to the oxidation activity. Rather, because the additive-added Cu–Na-ZSM-5 zeolites were calcined at 773 K for 2 h in a flowing gas mixture of oxygen and nitrogen, it seems reasonable to theorize that the active species, as the promoter, has the form of sodium oxide, similar to Na_2O; hence the oxidation activity was not primarily dependent on the anion parts of the additive, including the sodium cation. It is thus reasonable to consider the additives used in this study as precursors to the active promoter rather than as being the active species themselves. Since the behavior of the decomposition of the Na-including additives to the sodium oxide, such as NaOH and $NaNO_3$, are different from each other, the minor differences in the oxidation activity may be attributed in part to the degree of decomposition of the alkali cation including additives.

The results concerning the effect of alkali metal ion on the oxidation activity showed that the behavior of the oxidation activity was only slightly varied by the kind of alkali metal ion except for the lithium cation, whose ability as a promoter for oxidation was appreciably smaller than that of the other alkali metal ions. It is known (20) that the lithium cation has a much larger hydration energy than other alkali cations. The decomposition of LiOH to the corresponding lithium oxide, as an active promoter, may be more difficult than that of the other alkali metal ions.

It is of interest to investigate whether an additive like NaOH acts as a promoter in concert form with Cu ions or as an independent form. Since the $NaOH_{imp}$–Na-ZSM-5 zeolite, in contrast to the $NaOH_{imp}$–Cu–Na-ZSM-5 zeolite, had no promoted activity for oxidation, an additive such as NaOH is considered to function as a promoter for the oxidation of benzyl alcohol only in the presence of Cu ions. The oxidation activity of the $NaOH_{imp}$–Cu–Na-ZSM-5 had a maximum value at around 70–80% of the ion-exchange of the Cu ion. Using the Cu–Na-ZSM-5 zeolite without alkali additive as a catalyst, a similar catalytic behavior, thus a maximum Cu ion-exchange activity of ca. 80%, was obtained (21). Hence, the added NaOH seems to be directly connected to the oxidation function of the Cu ions, rather than to be an independent function of the NaOH. To further study the role of the added NaOH in benzyl alcohol oxidation, a physically mixed catalyst of NaOH-added Na-ZSM-5 and Cu–Na-ZSM-5 zeolites was used as a catalyst for benzyl alcohol oxidation. The physically mixed catalytic system of the NaOH-added Na-ZSM-5 and the Cu–Na-ZSM-5 was found to have a significantly smaller yield of benzaldehyde than the $NaOH_{imp}$–Cu–Na-ZSM-5 zeolite, though the yields of the deep oxidation products from both catalytic systems were almost the same. This result indicates that the added NaOH will act as a promoter for the oxidation if the NaOH could be more accessible to the Cu ions. The concerted function of the Cu ions and the added NaOH is thus considered to be a main factor favoring promoted activity in the parital oxidation of benzyl alcohol. The physically mixed catalyst was found to have a larger yield of benzaldehyde as compared to the Cu–Na-ZSM-5 zeolite (Table 4). This may also be interpreted by the Cu-alkali synergism that the part of the NaOH on the $NaOH_{imp}$–Na-ZSM-5 zeolite may migrate through space to the Cu–Na-ZSM-5 zeolite because of the ease of the evaporation of the alkali species, though we have no direct proof at the present stage.

It seems reasonable to assume that the benzyl alcohol is oxidized to benzaldehyde by Cu ions, which are considered to be the active species for the oxidation and have a redox function. The Cu(II) ions, which oxidized benzyl alcohol to benzaldehyde, will thus be reduced to Cu(I) ions (21). The reduced Cu(I) ions can be reoxidized by an oxygen molecule and/or its atom (21). In this case, oxygen acts as the oxidant for Cu(I) ions. Even in the absence of gaseous oxygen molecules, the partial oxidation product, benzaldehyde, could be synthesized with the Cu-Na-ZSM-5 catalyst regardless of the presence of the NaOH additive (Fig. 4). Under this reaction condition, the $NaOH_{imp}$–Cu–Na-ZSM-5 zeolite had an appreciably higher yield of benzaldehyde than the Cu–Na-ZSM-5 without NaOH. In contrast to the partial oxidation, no deep oxidation products were observed in the oxygen-free atmosphere. These results support the already described assumption (21, 27) that the oxygen species adsorbed on the Cu–Na-ZSM-5 zeolite with (or without) alkali will be responsible for the partial oxidation of benzyl alcohol, and no deep oxidation will occur without gaseous oxygen.

A Cu(I) ion, in contrast to a Cu(II) ion, has been reported to selectively interact with and adsorb a carbon monoxide molecule (22). Howard and his co-workers (23) have studied the IR spectra of the CO molecule adsorbed on a Cu(II)–NaY zeolite and have observed two IR absorption peaks. The absorption peaks at 2156 and 2140 cm^{-1} have been identified as CO–Cu(I) complexes situated in the SI and SII sites of the Y zeolite (23). More recently, two or more Cu species, which were in different ligand fields, in the Cu–Na-ZSM-5 zeolites have been suggested based on their ESR spectra (24–26). We have also reported (27) the redox behavior and mobility of the Cu ions in Cu ion-exchanged Na-ZSM-5 zeolites during oxidation of benzyl alcohol by the methods of CO adsorption, IR absorption measurement of CO adsorbed on the Cu–Na-ZSM-5, and diffuse reflectance spectra measurements. It has been reported (27) that there are at least two types of Cu species in the Cu–Na-ZSM-5 zeolite based on the observation of the IR spectra of the adsorbed CO, in agreement with the ESR spectra already reported in Ref. (24), and some of the Cu ions in the Cu–Na-ZSM-5 zeolite can be relocated from a recessed site (corresponds to a 2157 cm^{-1} IR peak of the adsorbed CO) to the channel section (corresponds to a 2138 cm^{-1} IR peak of the adsorbed CO) with the help of the withdrawing ability of an alcohol such as benzyl alcohol or ethanol. The Cu ions which can be geometrically displaced sites such as a channel intersection have been discussed (27) to be responsible to the oxidation, particularly partial oxidation of benzyl alcohol. The IR spectum of CO adsorbed on the Cu–Na-ZSM-5 with an alkali additive gave a main absorption peak at 2135 cm^{-1}, identified as CO molecules adsorbed on the Cu(I) ions, in contrast to a main IR peak at 2157 cm^{-1} for the Cu–Na-ZSM-5 without alkali. This observation of the IR spectra may suggest that the Cu ions in the alkali-added Cu–Na-ZSM-5 mainly locate at sites such as channel sections, which are considered for the reactant molecules to be more easily accessible and which are responsible for the oxidation (27). The total intensity of CO adsorbed on the $NaOH_{imp}$–Cu–Na-ZSM-5 was found to be smaller than that on the Cu–Na-ZSM-5 without NaOH. These results thus suggest that the Cu(I) ions in the $NaOH_{imp}$–Cu–Na-ZSM-5 evacuated at 773 K are lower than those in the corresponding Cu–Na-ZSM-5 without alkali pretreated under the same conditions. One of the roles of alkalis such as NaOH may be to make the Cu(I) ions more easily reoxidized.

An oxygen species, either in the associated molecular or the dissociated atomic state, is considered to directly participate in the reoxidation process of the reduced Cu(I) to Cu(II) ions. From the point of view of the activation of oxygen species, it is meaningful to investigate the catalytic activity of the $NaOH_{imp}$–Cu–Na-ZSM-5 zeolite for the exchange reaction of an oxygen molecule and compare it with the exchange activity of the Cu–Na-ZSM-5 without NaOH. The activity of $NaOH_{imp}$–Cu–Na-ZSM-5 for the $^{18}O_2$–$^{16}O_2$ exchange reactions was found to be appreciably greater than that of Cu–Na-ZSM-5 itself (Fig. 12). The Cu ions with alkali additives promote the dissociation of oxygen molecules; therefore the redox process of the Cu species can be considered to proceed more easily (28). Previously, we have reported (29) that a Cu(II)–NH_3 complex with an alkali ligand like OH^- has a higher oxidizing ability than that of the corresponding Cu(II) complex without the alkali from the comparison of energy values of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) based on a semiempirical molecular orbital calculation of these Cu complex's models. The alkali adjacent to the Cu ion in the Na-ZSM-5 zeolite will directly act as ligands for the Cu ion to promote the oxidation activity. The oxygen-exchange activity of the copper oxide has been reported (29) to be promoted by the addition of an alkali metal oxide. An alkali metal sulfate added V_2O_5 had also been found (30) to have a high activity for an exchange reaction between gas-phase and lattice oxygen species. As additives the alkalis can be reasonably considered to mainly function on the Cu species to promote oxidation activity rather than to function separately from the Cu ion.

The $NaOH_{imp}$–Cu–Na-ZSM-5 catalyst was found to have less accumulation of carbonaceous material than the Cu–Na-ZSM-5 itself. This may suggest that the part of the added alkalis deactivates the acid sites, which may be responsible for the formation of the carbon-like material, present on the zeolite. The adsorbed NH_3 in fact tended to decrease with an increase in the additive, as illustrated in Fig. 9. One of the roles of the added alkalis is thus to deactivate the acid site and to prevent the accumulation of coke-like materials during oxidation reaction.

CONCLUSIONS

The addition of alkali metal to a Cu–Na-ZSM-5 zeolite was found to promote its catalytic activity for benzyl alcohol oxidation, particularly the partial oxidation to produce benzaldehyde rather than the deep oxidation. The $\text{alkali}_{\text{imp}}$–Cu-Na-ZSM-5 catalyst had a maximum oxidation activity at around 80% of the Cu ion-exchange. Na, K, and Rb were found to act in a similar manner as promoters for benzyl alcohol oxidation. On the other hand, Li had lesser effect as a promoter for benzyl alcohol oxidation. The corresponding alkali metal oxides were suggested to act largely as promoters for benzyl alcohol oxidation since almost similar oxidative behaviors were observed using the alkali metal salts with the same alkali metal cations but with different anions, which were pretreated at 773 k for 3 h in air. The role of the added alkali near the Cu ions was found to be to promote the dissociation of oxygen molecules by Cu ions and it was suggested to participate indirectly in the partial oxidation of benzyl alcohol, in which the Cu ion and the added alkali cooperate with each other in the oxidation rather than functioning separately. The added alkali was also suggested to make Cu ions in the Na-ZSM-5 zeolite locate to sites that the reactant molecules can access more easily. The alkali was further found to prevent the deactivation of the Cu–Na-ZSM-5 zeolite by retarding the formation of carbonaceous materials on the zeolite surface.

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