FARADAY

Roles of alkali-metal added to Cu-NaZSM-5 catalysts in the oxidation of benzyl alcohol

Minoru Genta, Satoru Nishiyama, Shigeru Tsuruya* and Mitsuo Masai
Department of Chemical Science & Engineering, Faculty of Engineering, Kobe University, Nada Kobe 657, Japan

Alkali-metal addition to Cu-NaZSM-5 zeolite promotes oxidation activity (mainly partial oxidation rather than complete oxidation) using benzyl alcohol oxidation as a model reaction. The alkali-metal added to Cu-NaZSM-5 is present as the corresponding oxide, such as Na_2O. The percentage of Cu ion exchanged and the added Na/Cu atomic ratio in Na-added Cu-NaZSM-5 are important factors governing the oxidation activity. The added alkali-metal is suggested to be located in the neighbourhood of the Cu species as ligands, rather than covering the Cu species in Cu-NaZSM-5 zeolite. The influence of added Na on the adsorption and redox properties of Cu-NaZSM-5 zeolite were investigated to shed light on the role of the added alkali-metal during oxidation by means of ethanol and CO adsorptions, O_2 uptake, TPD of ethanol and temperature-programmed reaction, in addition to the results of the oxidation reaction. The amounts of O_2 uptake by the prereduced Na-added Cu-NaZSM-5 were considerably larger than those by the corresponding Cu-NaZSM-5 without alkali-metal. The added alkali-metal is considered to help accommodate the adsorbed oxygen species, which is dissociated and is responsible for the partial oxidation of benzyl alcohol. The added alkali-metal also allows the Cu^I species to be more easily oxidized and to adsorb greater amounts of reactant alcohol; this explains the promotion effect of the added alkali-metal observed in the gas-phase catalytic oxidation of benzyl alcohol.

Copper ion-exchanged zeolites such as Cu-NaY and Cu-NaZSM-5 have reversible redox properties[1–6] and have been tested as catalysts for various oxidation reactions[7–15] Cu ion-exchanged NaZSM-5 (Cu-NaZSM-5) catalytically decomposes NO molecules[16–25] which are considered to be one of the causes of acid rain and photo-oxidation. The reversible redox properties of Cu ions play an important role in the steady catalytic activity of NO decomposition.

The liquid-phase oxidative coupling reaction of 2,6-dimethylphenol to form the corresponding poly(phenylene oxide), which is one of the engineering plastics, has been reported by Hay *et al.* using a copper–amine complex catalysts.[26,27] A basic copper complex, which consists of copper(II) chloride and alkali such as KOH, has increased catalytic activity for the liquid-phase oxidative coupling reaction of a phenol derivative such as 2,6-dimethylphenol.[28–30] The alkali/Cu^{II} salt mole ratio greatly affects the selectivity of the oxidative coupling products, and therefore the C—O and C—C coupling products, of the phenol derivative, in addition to the oxidation activity.[28–30]

The synthesis and partial characterization of alkali-modified X and Y zeolites for use as base catalysts have been presented by Hathaway and Davis;[31,32] upon impregnation of Cs—NaX and Cs—NaY with identical loadings of caesium acetate, the catalyst activity manifested in the yield of acetone was an order of magnitude greater than that found for the Cs—NaX zeolite. Hathaway and Davis[33] have also reported on the catalytic activity in the alkylation of toluene with methanol using caesium acetate-modified Cs—NaY and Cs—NaX catalysts. The catalytic activity of a series of alkali-exchanged and alkali-impregnated ZSM-5 zeolites in the alkylation of toluene with methanol has been investigated.[34] The reaction pathways involved in the alkylation of toluene with methanol have been investigated by *in situ* IR spectra monitoring of the reaction process on the Cs—NaY impregnated with caesium acetate.[35] Alkali metals loaded into the corresponding cation-exchanged X zeolites by vapour generated from the azide, and the formation of alkali-metal particles in the zeolite have been studied by EPR and far-IR spectra.[36–38] Basicity in alkali-cation exchanged Y zeolites has been characterized by an X-ray photoelectron spectroscopy (XPS) study using pyrrole as a probe molecule.[39] The effects of alkali-metal hydroxide pretreatment on the hydrogenation activity of nickel-loaded Y-type zeolites have been studied by Coughlan and Keane;[40] the alkali-pretreated zeolites exhibit a uniquely high steady-state catalytic activity in the hydrogenation of benzene to cyclohexane. The effects of alkali addition to the transition metal ion were investigated using a supported copper[41] and cobalt[42] ion-exchanged Y. We have already reported that the alkali addition in the Cu ion-exchanged NaZSM-5 (Cu-NaZSM-5) zeolite caused a considerable increase in the catalytic activity of benzyl alcohol oxidation.[43,44] Note that the catalytic activity for partial oxidation, rather than full oxidation, increases on adding alkali to the Cu-NaZSM-5 zeolite. The alkali-metal added Cu-NaZSM-5 zeolite has also increased the catalytic activity for the $^{16}O_2$–$^{18}O_2$ exchange reaction.[43,44]

In the present study, we extend our investigation on the promotion effect a of the alkali-added Cu-NaZSM-5 zeolite and discuss the role of the alkali added to the Cu-NaZSM-5 zeolite on the catalytic activity for benzyl alcohol oxidation.

Experimental

Catalyst preparation

ZSM-5 zeolite was synthesized by a method similar to that in a patent.[45] The prepared Na type ZSM-5 zeolite was treated twice with 1 mol dm^{-3} $NaNO_3$ aqueous solution for 1 h at 342–358 K to guarantee 100% Na content in the prepared zeolite. After the Na ion treatment, the Na ZSM-5 zeolite was washed with deionized water, filtered, dried for more than 12 h, and calcined for 3 h at 773 K under an air atmosphere. Cu ion-exchanged NaZSM-5 (Cu-NaZSM-5) zeolite was prepared by a conventional ion-exchange method (2 h, 343–353 K) using an aqueous solution of a prescribed concentration of $Cu(CH_3CO_2)\cdot H_2O$ (Nacalai Tesque, guaranteed reagent). After the Cu ion-exchange, the obtained Cu-NaZSM-5 zeolite was filtered, dried for more than 12 h, and calcined for 3 h at

773 K under an air atmosphere. Analyses of the Si/Al atomic ratio and the amount of ion-exchanged Cu were carried out by an atomic absorption (AA) method using a Shimazu Model AA-630-01 AA spectrophotometer after each zeolite sample was homogeneously dissolved by adding one or two drops of neat hydrogen fluoride (Hashimoto Chemical, 47% content, guaranteed reagent). Alkali-metal and alkaline-earth metal added Cu-NaZSM-5 zeolites were prepared by an impregnation method using aqueous solutions of alkali and alkaline earth acetates followed by calcination at 773 K for 3 h.

Benzyl alcohol oxidation catalysed by alkali-added Cu-NaZSM-5

The gas-phase catalytic oxidation of benzyl alcohol was conducted under atmospheric pressure using a conventional fixed-bed Pyrex glass flow reactor with *ca.* 15 mm id. After 0.5 g of the zeolite catalyst was calcined for 2 h at 773 K in a mixed flow of oxygen and nitrogen (O_2/N_2 mole ratio = 1/4), benzyl alcohol was fed to the reactor through a micro-feeder at a prescribed temperature; this was considered to be the starting stage of the oxidation. Typical reaction conditions were as follows: $W/F = 21.7$ (g catalyst) min mol^{-1} (W, catalyst weight; F, total molar rate); partial pressure of $O_2 = 8.99 \times 10^3$ Pa; partial pressure of $N_2 = 8.69 \times 10^4$ Pa; partial pressure of benzyl alcohol = 2.73×10^4 Pa. The liquid-phase oxidation products and unreacted benzyl alcohol were trapped at 251 K using a mixture of carbon tetrachloride and liquid nitrogen. The liquified reaction mixture were diluted with 1 cm^3 of dimethylformamide (Nacalai Tesque, guaranteed grade reagent) and analysed by a gas chromatograph equipped with a flame ionization detector (Shimazu Type GC-4BM) with nitrogen (20 cm^3 min^{-1}) as a carrier gas using a 2 m length glass column (id 0.3 cm) packed with PEG HT and Uniport HP 5% (60–80 mesh) at 373–473 K. The gaseous products were also analysed by means of gas chromatography (Shimazu Model GC-4BM) with the intermediate-cell method[46] using a 1 m × 0.3 cm stainless-steel column packed with 5A molecular sieves (60–80 mesh) at 293 K with hydrogen as a carrier gas (35 cm^3 min^{-1}). The carbon balance of the oxidation mixture was generally more than 90%. The main oxidation products were benzaldehyde and carbon dioxide. The carbon balance, the conversion of benzyl alcohol, and the yields of benzaldehyde and CO_2 were defined as follows:

Carbon balance (%) =

$$\frac{\begin{array}{c}\text{moles of benzyl alcohol recovered}\\ +\ \text{moles of benzaldehyde produced}\\ +\ \tfrac{1}{7}[\text{moles of } CO_2 \text{ produced}]\end{array}}{\text{moles of benzyl alcohol fed}} \times 100$$

Conversion (%) =

$$\frac{\begin{array}{c}\text{moles of benzaldehyde produced}\\ +\ \tfrac{1}{7}[\text{moles of } CO_2 \text{ produced}]\end{array}}{\text{moles of benzyl alcohol fed}} \times 100$$

Yield of benzaldehyde (%) =

$$\frac{\text{moles of benzaldehyde produced}}{\text{moles of benzyl alcohol fed}} \times 100$$

$$\text{Yield of } CO_2 \text{ (\%)} = \frac{\tfrac{1}{7}[\text{moles of } CO_2 \text{ produced}]}{\text{moles of benzyl alcohol fed}} \times 100$$

Ethanol adsorption on the Na-added Cu-NaZSM-5 and the Cu-NaZSM-5 zeolites

The adsorption ability of the Na-added Cu-NaZSM-5 zeolite and its temperature dependence were investigated using ethanol as an adsorbate in place of benzyl alcohol because of its lower vapour pressure. The adsorption of ethanol was performed using conventional low-pressure type static gas adsorption equipment with greaseless bulbs. The amounts of all samples were 0.03 g. After the pretreatment of the sample at 773 K for 1 h under 20 kPa of O_2, the entire system was degassed at 363 K for 1 h. A 4.0 kPa portion of ethanol was introduced, and the total amount of ethanol adsorption was measured after the adsorption equilibrium was reached after 15 min. The measurement of ethanol adsorption (the amount of reversible adsorption) was repeated after degassing at 363 K for 1 h. The difference between the total amount of ethanol adsorption and the amount of reversible ethanol adsorption was estimated as the amount of the irreversible ethanol adsorption.

Temperature programmed desorption (TPD) of ethanol adsorbed on Na-added Cu-NaZSM-5 and Cu-NaZSM-5 zeolites

TPD of ethanol [variations in both the differential heat (reference; silica sand) and the sample weight by desorption of ethanol at the desorption temperatures] was performed using a thermal balance with differential thermal analysis equipment (Shimazu Model DTG-40 differential thermal and thermal weight analysis equipment) connected to a micro-feeder. After 10 mg of catalyst in the thermal balance cell was calcined at 773 K for 1 h in air atmosphere (30 cm^3 min^{-1}) and cooled at room temperature, the atmosphere in the balance was purged with pure N_2 gas. Ethanol (0.015 mol h^{-1}) in an N_2 gas stream (80 cm^3 min^{-1}) was supplied to the balance for 30 min. After a second purge with N_2 gas for 30 min, the TPD of ethanol under an N_2 stream (30 cm^3 min^{-1}) was started with a temperature increase rate of 20 K min^{-1}.

CO adsorption on Na-added Cu-NaZSM-5 and Cu-NaZSM-5 zeolites

CO adsorption on the catalyst was measured using semi-micro gas adsorption equipment made of capillary glass tubes. After the catalyst (usually 0.05 g) was calcined at 773 K for 1 h under 20 kPa O_2, the entire system was degassed at 773 K for 2 h under less than 0.1 Pa. The dead volume was measured by introducing 1.3 kPa Hc at room temperature followed by degassing (<0.1 Pa) the entire system for 1 h. After CO(2.3 kPa) was introduced and the adsorption equilibrium of the entire system was confirmed to be reached, the total amount of adsorption was measured. The amount of the reversible adsorption was measured by repeating the same operation after degassing at room temperature for 1 h. The difference between the amounts of the total and reversible adsorptions was considered as the amount of the irreversible adsorption.

Temperature-programmed reduction (TPR) of Na-added Cu-NaZSM-5 and Cu-NaZSM-5 zeolites

The relationship between the amount of H_2 consumption in the reduction of the catalyst and the reduction temperature was measured using reaction equipment connected to a gas chromatograph (Shimazu Model GC-4A with a TCD detector). The H_2O formed during the reduction was trapped in a glass trap tube which was cooled at 159 K (ethanol + liquid nitrogen coolant) and placed just before the TCD detector. A 0.4 g sample of the catalyst in a quartz-glass reactor was calcined at 773 K for 1 h in flowing air (50 cm^3 min^{-1}), cooled at room temperature, and the air flow was replaced with an N_2 flow (for 30 min). After the N_2 flow gas was replaced with a mixed gas [H_2 (4.82%) + N_2 (95.18%); 30 cm^3 min^{-1}] at room temperature, the temperature of the catalyst was increased at a constant rate (10 K min^{-1}).

Temperature-programmed oxidation (TPO) of ethanol catalysed by Na-added Cu-NaZSM-5 and Cu-NaZSM-5 zeolites

TPD of ethanol, used in place of benzyl alcohol because of its low vapour pressure, was performed using a differential thermal balance connected to a micro-feeder. A 0.04 g sample of catalyst placed in the balance cell was calcined at 773 K for 1 h in flowing air (30 cm^3 min^{-1}) and was cooled at room temperature. Ethanol was supplied at room temperature in the air flow (flow rate of the mixed gas, 80 cm^3 min^{-1}; ethanol, 0.08%; air, 99.92%), and the differential thermal and the weight changes during the reaction process were measured at a temperature increase rate of 20 K min^{-1}.

Measurement of the amount of O_2 uptake by reduced Na-added Cu-NaZSM-5 zeolite

The amount of O_2 consumed by a reduced catalyst was measured using semi-micro gas adsorption equipment made of capillary glass tubes. A 0.05 g sample of catalyst in a capillary sample tube, that was connected to the gas adsorption equipment, was calcined at 773 K for 1 h under O_2 atmosphere (20 kPa) and degassed (<0.1 Pa) at 773 K for 1 h. After CO was introduced at 20 kPa, the catalyst was treated at 773 K for 1 h, followed by degassing (<0.1 kPa) at 773 K for 1 h. After measurement of the dead volume of the sample cell by He introduction, O_2 (2.6 kPa) was introduced at 573 K, the sample was allowed to stand for 15 min, and the amount of total O_2 uptake was measured. Once again, O_2 (2.6 kPa) was introduced after degassing at 573 K for h, and the amount of the reversible O_2 uptake was measured. The difference between the amount of total and reversible O_2 uptakes was regarded as the amount of irreversible O_2 uptake.

Diffuse reflectance (DR) spectra of Na-added Cu-NaZSM-5 zeolite

The DR spectra of the catalysts were recorded with an electronic absorption spectrophotometer (Hitachi Model U-3210D) equipped with a 60Φ integral sphere (Hitachi Model 150-0902). The catalyst was mounted in an *in situ* cell, which consisted of sample-treating and sample-measuring parts and was connected to a vacuum line. The measured reflectance fractions were converted to Kubelka–Munk (KM) functions [$F(R)$] using a personal computer with an applied program.

XP spectra of Na-added Cu-NaZSM-5 zeolite

XP spectra of Na-added (added Na/Cu = 4) Cu-NaZSM-5 zeolites were measured to investigate the surface composition of the zeolite using a KRATOS Model XSAM 800 spectrometer [Al-Kα (1486.6 eV)]. The zeolite sample was incorporated in a thin indium plate, which was fixed on a sample holder. The binding energies of Na 1s and Cu 2p peaks were corrected on the basis of the Si 2p peak (103.3 eV) of the ZSM-5 zeolite framework. The Cu/Si and Na/Si atomic ratios on the surface of the sample were calculated using Data System DS 800 supplied by KRATOS.

Results

Gas-phase catalytic oxidation of benzyl alcohol catalysed by alkali- or alkaline-earth-added Cu-NaZSM-5 zeolites

We have already reported[43,44] that alkali added to Cu-NaZSM-5 zeolites caused an increase in the catalytic activity of benzyl alcohol oxidation performed at 673 K. At first, the effect of the alkali added to the Cu-NaZSM-5 zeolite was investigated at a relatively lower reaction temperature, 573 K. No product was detected in the oxidation of benzyl alcohol even at 673 K in the presence of only quartz sand without an alkali-added Cu-NaZSM-5 zeolite. The main products in the benzyl alcohol oxidation catalysed by the alkali-added Cu-NaZSM-5 zeolites were benzaldehyde, a partial oxidation product, and carbon dioxide, a complete oxidation product. No carbon monoxide was detected in the present reaction temperature of 573 K. Only a trace of benzene and/or toluene was produced under some reaction conditions.

The relationship between the conversion of benzyl alcohol and the time-on-stream during the benzyl alcohol oxidations at 573 K catalysed by Na (added Na/Cu atomic ratio, 4)-added Cu (Cu ion-exchanged %, 64)-NaZSM-5 [Na(4)-added Cu(64)-NaZSM-5] and Cu(64)-NaZSM-5 zeolites are illustrated in Fig. 1. The addition of an alkali-metal such as Na caused a remarkable increase in the oxidation activity. The degree of the deactivation of the Na-added Cu-NaZSM-5 catalyst during the oxidation was not very large even at a time-on-stream of 4 h.

The oxidation of benzyl alcohol was performed using various alkali- and alkaline-earth-metal-added Cu-NaZSM-5 zeolites (Table 1). All the atomic ratios of the added alkali- or alkaline-earth-metal to the Cu ion-exchanged were kept constant at four. The addition of an alkali-metal (Na, K, Rb and Cs but not Li) to the Cu-NaZSM-5 zeolite caused an increase in the yield of benzaldehyde and CO_2. The alkaline-earth metals Mg, Ca, Sr and Ba, had no effect on the promotion of the oxidation activity of the Cu-NaZSM-5 zeolite at a comparatively low reaction temperature (573 K). However, only Ba-added Cu(87)-NaZSM-5 had high oxidation activity at a reaction temperature of 673 K, although we have no explanation for this at present. We then studied in detail the oxidation activity, the redox and the adsorption properties of the Na-added Cu-NaZSM-5 zeolite as an alkali-added Cu ion-exchanged ZSM-5 zeolite.

The effect of the percentage of Cu ion exchanged in the Na(4)-added Cu-NaZSM-5 zeolite on the product yields in the benzyl alcohol oxidation was investigated at a reaction temperature of 573 K (Fig. 2). Both the yields of benzaldehyde and CO_2 increased with an increase in the percentage of the ion-exchanged Cu and had maximum values at a percentage of *ca.* 65%. Particularly, the yield of benzaldehyde began to increase abruptly at a percentage of exchanged Cu ion of *ca.* 50.

The influence of the added Na amount on both the yields of benzaldehyde and CO_2 was investigated at 573 K (Fig. 3). The benzaldehyde yield increased with an increase in the amount

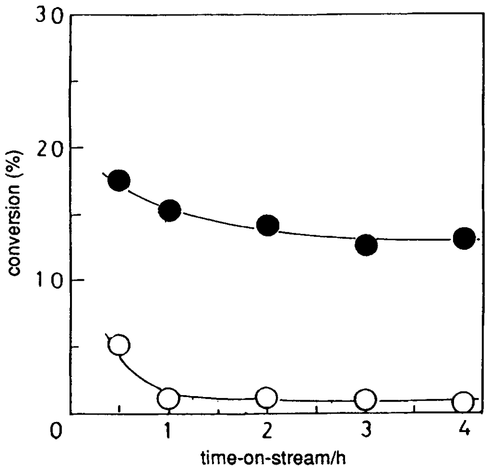

Fig. 1 Relationship between conversion *vs.* process time in the benzyl alcohol oxidation. Reaction temperature, 573 K; catalyst, 0.5 g; $W/F = 21.7$ (g catalyst) min mol^{-1}; partial pressure of $N_2 = 8.99 \times 10^4$ Pa; partial pressure of $O_2 = 8.69 \times 10^3$ Pa; partial pressure of benzyl alcohol = 2.73×10^3 Pa; ●, Na(4)-added Cu(64)-NaZSM-5 (Si/Al = 40); ○, Cu(64)-NaZSM-5.

Table 1 Benzyl alcohol oxidation catalysed by alkali-metal and alkaline-earth-metal added Cu-NaZSM-5 zeolites[a]

catalyst[b]	reaction temperature/K	conversion (%)	benzaldehyde yield (%)	CO_2 yield (%)
Cu(64)-NaZSM-5	573	0.3	0.1	0.2
Cu(87)-NaZSM-5	673	10.5	4.1	6.4
Li(4)-added Cu(64)-NaZSM-5	573	11.4	11.4	0.0
Na(4)-added Cu(64)-NaZSM-5	573	13.6	11.4	2.2
K(4)-added Cu(64)-NaZSM-5	573	28.9	22.9	6.0
Rb(4)-added Cu(64)-NaZSM-5	573	8.6	7.7	0.9
Cs(4)-added Cu(64)-NaZSM-5	573	16.4	14.7	1.7
Mg(4)-added Cu(64)-NaZSM-5	573	0.4	0.4	0.0
Mg(4)-added Cu(64)-NaZSM-5	673	6.5	4.2	2.3
Ca(4)-added Cu(64)-NaZSM-5	573	0.4	0.4	0.0
Ca(4)-added Cu(64)-NaZSM-5	673	7.5	4.2	3.3
Sr(4)-added Cu(64)-NaZSM-5	573	0.3	0.3	0.0
Sr(4)-added Cu(64)-NaZSM-5	673	9.8	5.4	4.4
Ba(4)-added Cu(64)-NaZSM-5	573	0.6	0.6	0.0
Ba(4)-added Cu(64)-NaZSM-5	673	33.0	21.0	12.0

[a] Si/Al atomic ratio, 40 for Cu(64)-NaZSM-5 and 48 for Cu(87)-NaZSM-5; catalyst, 0.5 g; *W*/*F*, 21.7 g catalyst min mol^{-1}; N_2 partial pressure, 8.99 × 10^4 Pa; O_2 partial pressure, 8.69 × 10^3 Pa; partial pressure of benzyl alcohol, 2.73 × 10^3 Pa. [b] Both alkali metals and alkaline-earth metals were added as acetate salts.

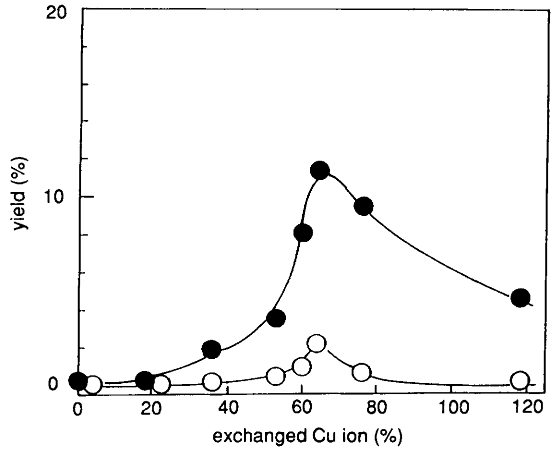

Fig. 2 Influence of percentage of Cu ion-exchange on the yields of the oxidation products. Catalyst, 0.5 g of Na(4)-added Cu-NaZSM-5 (Si/Al = 40); Reaction temperature, 573 K; catalyst, 0.5 g; *W*/*F* = 21.7 (g catalyst) min mol^{-1}; partial pressure of N_2 = 8.99 × 10^4 Pa; partial pressure of O_2 = 8.69 × 10^3 Pa; partial pressure of benzyl alcohol = 2.73 × 10^3 Pa; ●, benzaldehyde; ○, CO_2.

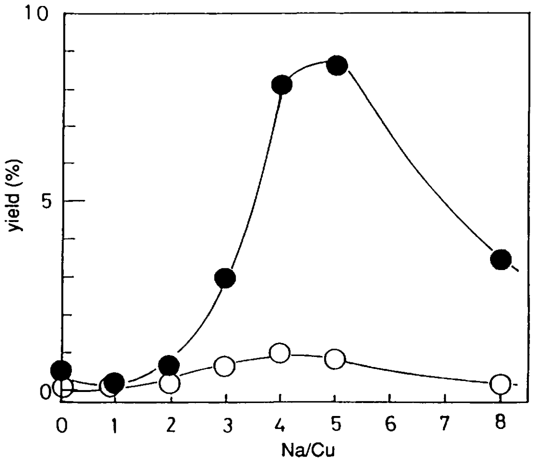

Fig. 3 Influence of added Na amount on the yields of the oxidation products. Catalyst, 0.5 g of Na(4)-added Cu-NaZSM-5 (Si/Al = 40); Reaction temperature, 573 K; catalyst, 0.5 g; *W*/*F* = 21.7 (g catalyst) min mol^{-1}; partial pressure of N_2 = 8.99 × 10^4 Pa; partial pressure of O_2 = 8.69 × 10^3 Pa; partial pressure of benzyl alcohol = 2.73 × 10^3 Pa; ●, benzaldehyde; ○, CO_2.

of added Na and had a maximum value at an Na/Cu atomic ratio of *ca.* 4–5. Similar behaviour was observed in the relationship between the CO_2 yield and the added Na amount, although the degree of the increase in the CO_2 yield was considerably smaller than that in benzaldehyde (Fig. 3). The alkali added to the Cu-NaZSM-5 zeolite therefore promoted the oxidation activity of benzyl alcohol, particularly the catalytic activity of the partial oxidation.

To investigate the role of the added alkali-metal the difference in the effects between the alkali metals added to Cu-NaZSM-5 zeolite and to NaZSM-5 zeolite on the catalytic activity in the benzyl alcohol oxidation was studied (Table 2). The Na added to the NaZSM-5 without a Cu ion did not promote benzyl alcohol oxidation, in contrast to the influence of the Na addition to Cu-NaZSM-5 zeolite. The alkali-metal itself, such as Na, thus seems to have no effect on the oxidation and to promote the oxidation activity only in coexistence with a Cu ion.

Some sodium salts with different kinds of anions were used as the alkali-metal additive for the Cu-NaZSM-5 zeolite in order to investigate the influence of anions on the yields of both benzaldehyde and CO_2 in the benzyl alcohol oxidation (Table 3). All the sodium salts added to Cu-NaZSM-5 catalysts promoted the oxidation of benzyl alcohol. The effect of the calcination temperature on sodium acetate added to Cu-NaZSM-5 zeolite was investigated using DTA-TG equipment (Fig. 4). An exothermic peak based on the decomposition (combustion) of the acetate moiety[31] was observed (Fig. 4b) at *ca.* 573 K, accompanying weight loss of the catalyst in the TG analysis, using the zeolite without precalcination. However, the Na-added Cu-NaZSM-5 zeolite precalcined at 773 K for 3 h had no corresponding DTA peak (Fig. 4d). The added sodium acetate is thus considered to be present as the corre-

Table 2 Effect of sodium addition on benzyl alcohol oxidation[a]

catalyst	benzaldehyde yield (%)	CO_2 yield (%)
NaZSM-5	0.2	0.0
Na-added NaZSM-5	0.3	0.0
Cu(64)-NaZSM-5	0.7	0.2
Na(4)-added Cu(64)-NaZSM-5	11.4	2.2

[a] Catalyst, 0.5 g (Si/Al = 40); added Na amount (as sodium acetate), 2.9 × 10^{-4} mol (g catalyst)$^{-1}$ (added Na/Cu = 4); *W*/*F* = 21.7 (g catalyst) min mol^{-1}; N_2 partial pressure, 8.99 × 10^4 Pa; O_2 partial pressure, 8.69 × 10^3 Pa; partial pressure of benzyl alcohol, 2.73 × 10^3 Pa; reaction temperature, 573 K.

Table 3 Effect of sodium salts as additives for Cu(75)-NaZSM-5 on benzyl alcohol oxidation[a]

sodium salts	benzaldehyde yield (%)	CO_2 yield (%)
no added alkali	0.7	0.0
$NaNO_3$	5.8	0.9
CH_3COONa	9.5	0.7
NaOH	9.6	1.0
$NaHCO_3$	11.6	1.0

[a] Catalyst, 0.5 g of Cu(75)-NaZSM-5 (Si/Al = 40); added Na/Cu = 4; $W/F = 21.7$ (g catalyst) min mol^{-1}; N_2 partial pressure, 8.99×10^4 Pa; O_2 partial pressure, 8.69×10^3 Pa; partial pressure of benzyl alcohol, 2.73×10^3 Pa, reaction temperature, 573 K.

sponding oxide, Na_2O, in the Cu-NaZSM-5 zeolite after pretreatment at 773 K for 3 h in an air atmosphere.

To investigate the effect of oxygen on the oxidation of benzyl alcohol, oxidation in the presence and absence of gaseous oxygen was followed as illustrated in Fig. 5. After the steady-state operation (Fig. 5, region I) using Na(5)-added Cu(60)-NaZSM-5 zeolite as a catalyst in the presence of oxygen, the supply of oxygen was interrupted (Fig. 5, region II) followed by observation of the yield of oxidation products with process time. CO_2 production was entirely inhibited immediately after halting the oxygen supply. However, a yield of benzaldehyde was observed even in the absence of gaseous oxygen. Cu-NaZSM-5 catalyst without an alkali metal such as Na also shows similar behaviour for the oxidation of benzyl alcohol,[4,6] though the yield of benzaldehyde was considerably smaller than that oxidized by the Na-added Cu-NaZSM-5 catalyst used in this study. To investigate the possibility that the benzaldehyde observed during the absence of gaseous oxygen may be that produced during the oxygen supply followed by adsorption on the catalyst and elution from the catalyst to the gas phase, interruption of the benzyl alcohol supply was conducted as shown in Fig. 5 (region III). Neither oxidation product was observed under the mixed flow of molecular oxygen and nitrogen, and so the benzaldehyde observed during the absence of gaseous oxygen will be considered to be that oxidized by the oxygen species adsorbed on the Na-added Cu-NaZSM-5, rather than by gaseous oxygen itself. Note that re-oxidation treatment of the catalyst caused almost complete recovery of the oxidation activity (Fig. 5, region IV).

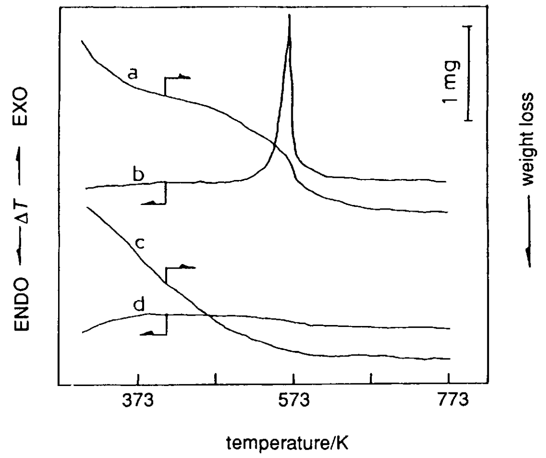

Fig. 4 DTA-TG spectra of Na-added Cu-NaZSM-5 (Si/Al = 40). Rate of temperature increase, 20 K min^{-1}; calcination, 773 K for 3 h under air flow (30 cm^3 min^{-1}); a, TGA spectrum of uncalcined Na(4)-added Cu(57)-NaZSM-5; b, DTA spectrum of uncalcined Na(4) added Cu(57)-NaZSM-5; c, TGA spectrum of calcined Na(4)-added Cu(57)-NaZSM-5; d, DTA spectrum of calcined Na(4)-added Cu(57)-NaZSM-5.

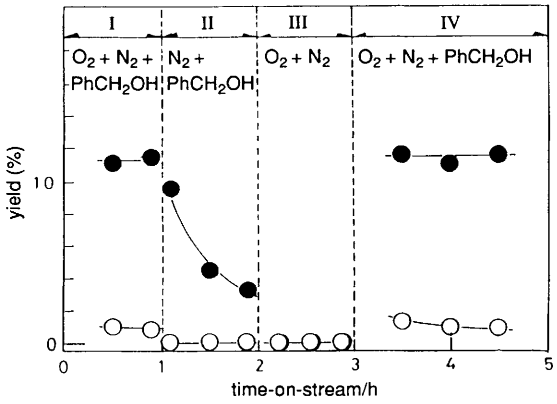

Fig. 5 Behaviour of benzyl alcohol oxidation under a nitrogen atmosphere. Catalyst, 0.5 g of Na(4)-added Cu-NaZSM-5 (Si/Al = 40); reaction temperature, 573 K; $W/F = 21.7$ (g catalyst) min mol^{-1}; partial pressure of $N_2 = 8.99 \times 10^4$ Pa; partial pressure of $O_2 = 8.69 \times 10^3$ Pa; partial pressure of benzyl alcohol = 2.73×10^3 Pa; ●, benzaldehyde; ○, CO_2.

Interaction between Na-added Cu-NaZSM-5 zeolite and ethanol

The interaction between Na-added Cu-NaZSM-5 zeolite and a reactant alcohol was investigated using ethanol as the reactant, instead of benzyl alcohol, because of the lower vapour pressure of the former. Alkali-metal addition to Cu-NaZSM-5 zeolite caused an increase[47] in the oxidation activity of the gas-phase catalytic oxidation of both ethanol and benzyl alcohol. It is therefore reasonable to discuss the role of the added alkali metal as a promoter of benzyl alcohol oxidation on the basis of the results obtained using ethanol, instead of benzyl alcohol.

The addition of Na (added Na/Cu = 4) to Cu(76)-NaZSM-5 zeolite increased the amount (2.8×10^{-4} mol (g catalyst)$^{-1}$) of irreversible adsorption of ethanol at 363 K in comparison with that (2.5×10^{-4} mol (g catalyst)$^{-1}$) by the Cu-NaZSM-5 zeolite without alkali metal. The amounts of the irreversible adsorption of ethanol on both the Na-added NaZSM-5 and the NaZSM-5 zeolites were 2.5 and 2.6×10^{-4} mol (g catalyst)$^{-1}$, respectively, indicating that an alkali metal such as Na does not affect ethanol adsorption on NaZSM-5 zeolite without Cu ions.

After ethanol adsorption on Na(4)-added Cu(76)-NaZSM-5 and Cu(76)-NaZSM-5 zeolites, TPD of ethanol was performed using DTA and TG methods (Fig. 6). An endothermic peak was observed, at *ca.* 543 K, accompanying a weight loss in the TPD of ethanol adsorbed on the Cu-NaZSM-5 (Fig. 6c, d). This endothermic peak is considered to be due to the desorption of weakly adsorbed ethanol or dehydration of adsorbed ethanol molecules, although the identification of the desorbed species was not performed at the present stage. The TPD of ethanol adsorbed on Na(4)-added Cu(76)-NaZSM-5 zeolite, which was pretreated at 773 K for 1 h under an air atmosphere, did not give the endothermic DTA peak observed in the TPD of ethanol adsorbed on Cu-NaZSM-5 zeolite (Fig. 6a, b). The addition of sodium to the Cu-NaZSM-5 catalyst also inhibits the dehydration of ethanol in the presence of oxygen.[47] The exothermic region was observed at more than *ca.* 550 K even in the absence of gaseous O_2 in the TPD of ethanol adsorbed on Na(4)-added Cu(76)-NaZSM-5, though the weight loss in this region was ambiguous. The assumption described previously that the oxygen species pre-adsorbed on the catalyst acts as the oxidant for benzyl alcohol oxidation under gaseous oxygen-free conditions is supported by this observation. The differences between the TPD spectra of ethanol adsorbed on the Na-added Cu-NaZSM-5 and the Cu-NaZSM-5 were thus consistent with the difference in the

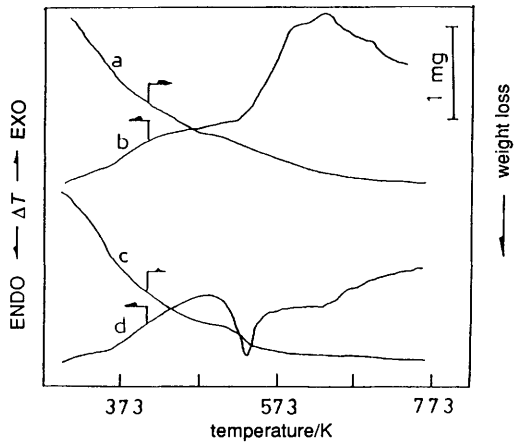

Fig. 6 TPD spectra of ethanol adsorbed on Na(4)-added Cu(76)-NaZSM-5 (Si/Al = 40) and Cu(76)-NaZSM-5 zeolites. TPD measurement, under N_2 flow (30 cm^3 min^{-1}); temperature-programmed rate, 20 K min^{-1}; catalyst pretreatment, calcined at 773 K for 30 min under air flow (30 cm^3 min^{-1}) followed by treatment at room temperature for 30 min under N_2 flow (30 cm^3 min^{-1}); ethanol, adsorbed at room temperature for 30 min in a mixed flow of ethanol and N_2 (80 cm^3 min^{-1}) followed by flowing N_2 (30 cm^3 min^{-1}) at room temperature for 30 min; a, TGA on Na(4)-added Cu(76)-NaZSM-5; b, DTA on Na(4)-added Cu(76)-NaZSM-5; c, TGA on Cu(76)-NaZSM-5; d, DTA on Cu(76)-NaZSM-5.

results of benzyl alcohol oxidation catalysed by both Na-added Cu-NaZSM-5 and Cu-NaZSM-5 zeolites.

Redox behaviour of Cu ions in Na-added Cu-NaZSM-5 zeolite

The Cu^{II} ion in ZSM-5 zeolite is easily reduced to Cu^{I} by evacuating the Cu^{II} ion-exchanged ZSM-5 zeolite at high temperature.[4] The redox behaviour of the Cu ions in both Na(2)-added Cu(60)-NaZSM-5 and Cu(60)-NaZSM-5 was investigated by CO adsorption, which selectively occurs only on Cu^{I}.[48] The increase in the evacuation temperature of both the zeolites tended to cause an increase in the amount of CO adsorption, though the CO adsorption amount on Na-added Cu-NaZSM-5 zeolite tended to be smaller than that on Cu-NaZSM-5 zeolite; the relationship between of the amount of CO adsorption *vs.* the evacuation temperature on Cu-NaZSM-5 zeolite indicates a stepwise shape (Fig. 7).

The dependence of the amount of CO adsorption on the amount of the Na added to Cu(60)-NaZSM-5, which was evacuated at 773 K for 2 h, was investigated (Fig. 8). After the CO adsorption amount reached a maximum at an atomic ratio of Na/Cu of *ca.* 1, the amount of the CO adsorption steadily decreased with an increase in the Na/Cu ratio.

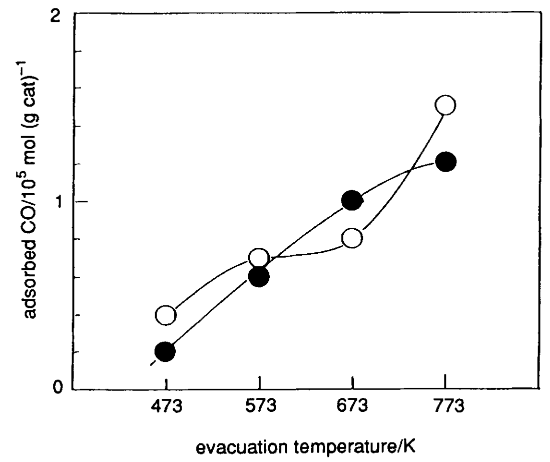

Fig. 7 Influence of evacuation temperature on the amount of CO adsorption. Adsorption temperature, 293 K; catalyst pretreatment, evacuated at 773 K for 30 min followed by treatment at 773 K for 1 h under oxygen atmosphere and evacuation at the prescribed temperature for 2 h; ●, Na(2)-added Cu(60)-NaZSM-5 (Si/Al = 40); ○, Cu(60)-NaZSM-5.

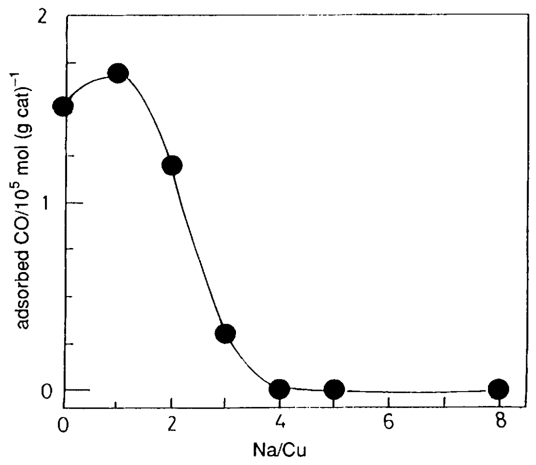

Fig. 8 Influence of added Na amount on the amount of CO adsorption. Catalyst, Na-added Cu(60)-NaZSM-5 (Si/Al = 40); adsorption temperature, 293 K; catalyst pretreatment, evacuated at 773 K for 30 min followed by treatment at 773 K for 1 h under oxygen atmosphere and evacuating at 773 K for 2 h.

TPR of the Cu ions in Na(4)-added Cu(76)-NaZSM-5 and Cu(76)-NaZSM-5 zeolites was measured using H_2 as a reducing agent to investigate the characterization of the reduction of the Cu ions in both zeolites (Fig. 9). The TPR spectrum of Cu(76)-NaZSM-5 consists of two distinctly separated peaks at 543 and 753 K (Fig. 9*b*). The TPR spectrum of Na-added Cu-NaZSM-5 zeolite had a broad peak at *ca.* 573–773 K, with a shoulder peak at *ca.* 723 K. The added Na may play a role in reducing the Cu ions more uniformly; in other words, it redistributes the Cu ions in the zeolite more uniformly, if the two peaks observed for TPR of Cu(76)-NaZSM-5 are identified as the Cu ions present at different sites and/or states in the NaZSM-5 zeolites.[49] The amount of H_2 uptake increased on adding Na based on the comparison of the total areas of the TPR peaks of both Na(4)-added Cu(76)-NaZSM-5 and Cu(76)-NaZSM-5 (area ratio of former to latter; 1 : 0.8). Thus the reduction behaviour of Cu ions in NaZSM-5 zeolite varied considerably on adding an alkali metal. The comparison of the lowest temperature at the H_2 uptake in both the Cu-NaZSM-5 zeolites with and without

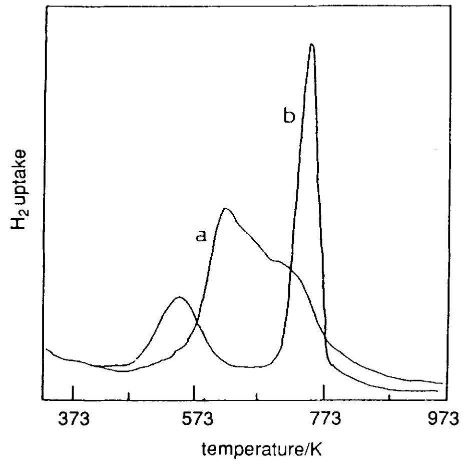

Fig. 9 TPR spectra of Na-added Cu-NaZSM-5 (Si/Al = 40) and Cu-NaZSM-5 zeolites. Temperature-programmed rate, 10 K min^{-1}; measured atmosphere, mixed flow gas (30 cm^3 min^{-1}) of 5.0% H_2 and 95.0% N_2; catalyst pretreatment, calcined at 773 K for 1 h under air atmosphere (50 cm^3 min^{-1}) followed by treatment at room temperature for 1 h under N_2 flow (50 cm^3 min^{-1}); a, Na(4)-added Cu(76)-NaZSM-5 (Si/Al = 40); b, Cu(76)-NaZSM-5.

Na suggests that the addition of Na makes it difficult for the Cu in the NaZSM-5 zeolite to be reduced at the lower temperature.

TPO of ethanol catalysed by Na(4)-added Cu(76)-NaZSM-5 and Cu(76)-NaZSM-5 zeolites was performed using DTA-GT equipment (Fig. 10). Very exothermic behaviour was observed at > *ca.* 673 K in the Cu(76)-NaZSM-5 catalytic system (Fig. 10d). On the other hand; the TPO of ethanol catalysed by Na(4)-added Cu(76)-NaZSM-5 zeolite displayed exothermic behaviour at $\gtrsim$573 K. Both types of exothermic behaviour mentioned here are considered to be due to the oxidation of ethanol. The Na-added Cu-NaZSM-5 catalyst thus had oxidation activity at lower temperatures than the Cu-NaZSM-5 zeolite without added alkali metal.

The O_2 uptake ability of Na(4)-added Cu-NaZSM-5 zeolite pretreated with CO at 773 K, in which some of the Cu ions are considered to be reduced to Cu^I, was investigated. The effect of the observed temperature on the amount of O_2 uptake of both Na(4)-added Cu(87)-NaZSM-5 and Cu(87)-NaZSM-5 zeolites is illustrated in Fig. 11. The O_2 uptake increased with an increase in the observed temperature of the Na-added Cu-NaZSM-5 zeolite even at a relatively low observed temperature, in contrast to that of Cu-NaZSM-5 zeolite without alkali metal added. The relationship between the Na/Cu atomic ratio of the Na-added Cu(60)-NaZSM-5, which was pretreated by degassing and CO treatment at 773 K, and the amount of the O_2 uptake is illustrated in Fig. 12. The amount of O_2 uptake abruptly increased at an atomic ratio of *ca.* 3–4, although it tended to level off at atomic ratios of >4.

DR spectrum of Na-added Cu-NaZSM-5 zeolite

The DR spectrum of Na(4)-added Cu(76)-NaZSM-5 zeolite, which was calcined at 773 K for 1 h, was observed at room temperature, in comparison with the DR spectrum of Cu(76)-NaZSM-5 zeolite without added alkali (Fig. 13). The DR spectrum of the Cu(76)-NaZSM-5 zeolite showed peaks at 320, 440 and >600 nm, in addition to the peaks at 250–300 nm, in accordance with the spectra reported previously.[6] The intensity of the KM function of Na-added Cu-NaZSM-5 zeolite tended to decrease at all observed wavelengths. Notably, the peak at 440 nm almost completely disappeared when Na was added to Cu-NaZSM-5 zeolite. The peak at 440 nm was identified as $Cu^I—O—Cu^I$ or $(Cu—O—Cu)^{2+}$ species.[20] This

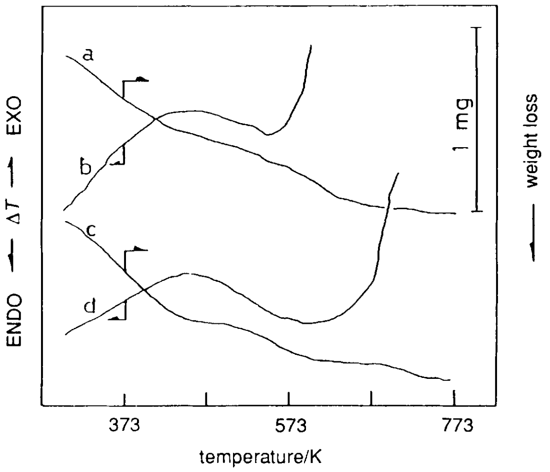

Fig. 10 TPO of ethanol catalysed by Na-added Cu-NaZSM-5 (Si/Al = 40) and Cu-NaZSM-5 zeolites. Temperature-programmed rate, 20 K min^{-1}; measured atmosphere, mixed flow gas (80 cm^3 min^{-1}) of 0.08% ethanol and 99.2% air; catalyst pretreatment, treated at 773 K for 1 h under air flow (80 cm^3 min^{-1}); a, TGA spectrum of Na(4)-added Cu(76)-NaZSM-5; b, DTA spectrum of Na(4)-added Cu(76)-NaZSM-5; c, TGA spectrum of Cu(76)-NaZSM-5; d, DTA spectrum of Cu(76)-NaZSM-5.

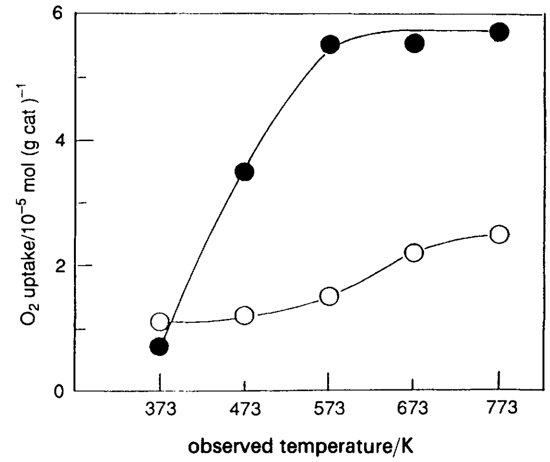

Fig. 11 Influence of observed temperature on the amount of O_2 uptake. Catalyst pretreatment, after the evacuation at 773 K for 30 min followed by treating at 773 K for 1 h under O_2 atmosphere and evacuating at 773 K for 1 h, treated with CO at 773 K for 1 h followed by evacuating at 773 K for 1 h; ●, Na(4)-added Cu(87)-NaZSM-5 (Si/Al = 48); ○, Cu(87)-NaZSM-5.

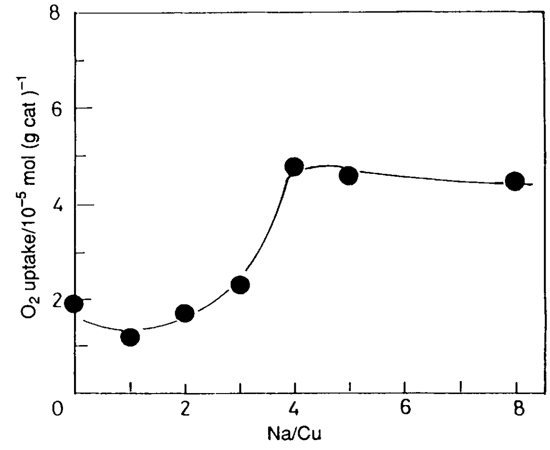

Fig. 12 Influence of added Na on the amount of O_2 uptake. Measured temperature, 573 K; catalyst pretreatment; after the evacuation at 773 K for 30 min followed by treating at 773 K for 1 h under O_2 atmosphere and evacuating at 773 K for 1 h, treated with CO at 773 K for 1 h followed by evacuating at 773 K for 1 h; Na-added Cu(60)-NaZSM-5 (Si/Al = 40).

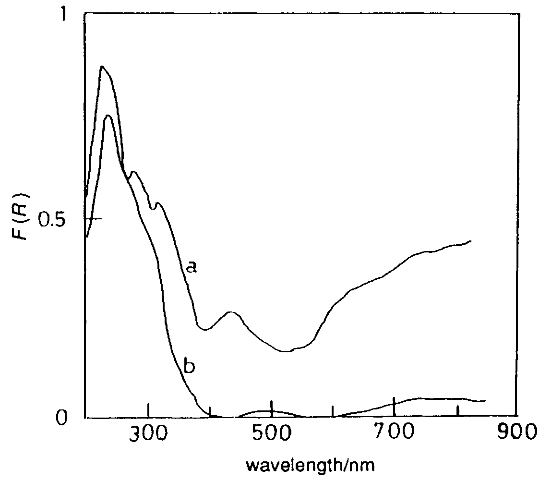

Fig. 13 DR spectra of Na(4)-added Cu(76)-NaZSM-5 (Si/Al = 40) and Cu(76)-NaZSM-5 zeolites. After degassing at 773 K for 30 min, both catalysts were oxidized at 773 K for 1 h under oxygen atmosphere followed by degassing at room temperature and measuring at room temperature; a, Cu(76)-NaZSM-5 (Si/Al = 40); b, Na(4)-added Cu(76)-NaZSM-5.

observation of the peak based on the dinuclear Cu^I species disappearing with Na addition suggests that the Cu^I species are easily re-oxidized by adding an alkali metal to Cu-NaZSM-5 zeolite, in agreement with the results obtained in the TPO measurements (Fig. 10).

Discussion

Alkali metals added to Cu-NaZSM-5 zeolite promoted the oxidation activity of benzyl alcohol. However, alkaline-earth metals added to Cu-NaZSM-5 zeolite had no effect on the catalytic activity of benzyl alcohol oxidation, though added Ba served as a promoter for the oxidation of benzyl alcohol at a higher reaction temperature. The active species of the added alkali metal is considered to be the corresponding oxide, such as Na_2O, on the basis of the DTA-TG analysis of the alkali metal salts on Cu-NaZSM-5 zeolite (Fig. 4); the reaction results in oxidation activities which were similar even if alkali-metal salts with different anions were used as the additive for Cu-NaZSM-5 (Table 3). Na added to NaZSM-5 did not promote the oxidation (Table 2). This result indicates that the added alkali-metal functions as a promoter for the catalytically active Cu species, rather than as an active species.

The yield of benzaldehyde had a maximum value at a Cu ion-exchange of *ca.* 65%. A similar relationship between the yield of benzaldehyde and the percentage of Cu ion-exchange has been reported for the benzyl alcohol oxidation catalysed by Cu-NaZSM-5.[4] The redox properties and displacement of Cu species in ZSM-5 type zeolites are dependent on the percentage of Cu ion-exchange as discussed previously,[6] these will again be applied to the present Na-added Cu-NaZSM-5 catalytic system in order to determine the maximum value of the oxidation activity. Cu species ion-exchanged at higher Cu percentages may thus relocate to a more open site, which is considered to be more accessible to a reactant.

The atomic ratio of Na added to Cu-NaZSM-5 zeolite to Cu ion-exchanged had an optimum value of *ca.* 4–5 for the benzyl alcohol oxidation (Fig. 3). Too much added Na in relation to the Cu retarded the oxidation activity. To investigate the surface state of the Na added to Cu-NaZSM-5, XP spectra of the Na and Cu species were measured on the basis of the Si atoms in the zeolite, focussed on the surface atomic ratios. The relative Cu/Si atomic ratios of Na (added Na/Cu = 4)-added Cu(75)-NAZSM-5 and Cu(75)-NaZSM-5 zeolites were 0.014 and 0.015, respectively, in spite of the observation that the Na/Si atomic ratio of both zeolites were 0.15 and trace, respectively. The XPS result suggests that the Cu species is not covered by the added alkali metal such as Na_2O which may be located in the neighbourhood of the Cu species, such as ligands for the Cu species.

Na-added Cu-NaZSM-5 zeolite under an N_2 atmosphere without gaseous O_2, after the steady state in the benzyl alcohol oxidation under gaseous O_2, gave considerable yields of benzaldehyde, though no CO_2 was produced, as illustrated in Fig. 5. Similar behaviour of the benzaldehyde yield in the absence of gaseous O_2 has been observed using the Cu-NaZSM-5 zeolite without added alkali metal, though the yields of benzaldehyde were considerably smaller than those in the present catalytic system.[4] These results suggest that the oxygen species adsorbed on the Na-added Cu-NaZSM-5 zeolite, rather than gaseous O_2 molecules, is responsible for the formation of benzaldehyde. The amount of O_2 uptake at more than 373 K by the Na-added Cu-NaZSM-5 zeolite, which was prereduced[4,6] by evacuating at 773 K for 1 h followed by treatment with CO at 773 K for 1 h, were considerably larger than those by the Cu-NaZSM-5 without alkali metal (Fig. 11). The O_2 uptake at 573 K of the Na-added Cu-NaZSM-5 also abruptly increases at added Na/Cu atomic ratios of *ca.* 4–5 (Fig. 12). The suggestion that the adsorbed oxygen species can mainly participate in the partial oxidation of benzyl alcohol and the observation that the Na-added Cu-NaZSM-5 zeolite which was prereduced could accommodate more oxygen species than the corresponding Cu-NaZSM-5 zeolite without alkali metal indicate that one of the roles of the added alkali metal is to help accommodate the absorbed oxygen species which is responsible for the partial oxidation of benzyl alcohol. The amount of ethanol adsorption was larger on the Na-added Cu-NaZSM-5 zeolite than on the Cu-NaZSM-5 itself, though the difference was not great. The alkali metal, in cooperation with the Cu species, may help the reactant alcohol to be adsorbed more strongly on the catalyst and to be oxidized to the corresponding aldehyde as supported by the comparison of the TPD spectra of ethanol on both the Na-added Cu-NaZSM-5 and the Cu-NaZSM-5 zeolites (Fig. 6).

The alkali metal addition caused a decrease in the amount of absorbed CO on the Na-added Cu-NaZSM-5 zeolite which was evacuated at 773 K (Fig. 7 and 8). These results on the CO adsorption may indicate that the Cu ions in the alkali-metal-added Cu-NaZSM-5 zeolite can be more stably present as Cu^{II} ions than in the Cu-NaZSM-5 without alkali metal. The comparison of the TPR spectra of the Na-added Cu-NaZSM-5 and the Cu-NaZSM-5 zeolites (Fig. 9) also seems to support the observation that the Cu^{II} ions are more stable in the alkali-metal-added Cu-NaZSM-5 than in the Cu-NaZSM-5. The TPO of ethanol in the presence of oxygen catalysed by the Na-added Cu-NaZSM-5 zeolite (Fig. 10) showed that the oxidation activity was promoted even at lower temperature (*ca.* 573 K), in contrast to the result of the TPO catalysed by the Cu-NaZSM-5 zeolite without alkali metal, in which the oxidation reaction tended to start at *ca.* 673 K. These results may suggest that the Cu ion reduced during the benzyl alcohol oxidation can be more easily re-oxidized in the alkali-metal-added Cu-NaZSM-5 zeolite. One of the roles of the added alkali metal is considered to be the promotion of the re-oxidation step of Cu^I to Cu^{II} in Cu-NaZSM-5 zeolite.

The uptake amount of O_2 in Na-added Cu-NaZSM-5 zeolite, which was pretreated with CO at elevated temperature, increased with an increase in the pretreatment temperature and levelled off at *ca.* 573 K. The Cu-NaZSM-5 zeolite without alkali-metal pretreated by the same method had a considerably lower amount of O_2 uptake and the O_2 uptake levelled off at *ca.* 773 K. The ability of O_2 adsorption on Ag-impregnated γ-alumina has been reported to increase on adding K^+ salt.[50] We have already reported[43,44] that the rate of the oxygen exchange reaction of $^{16}O_2$–$^{18}O_2$ catalysed by Cu-NaZSM-5 zeolite increases on adding a sodium salt, from which the added alkali metal is inferred to facilitate the dissociation of an O_2 molecule. The larger O_2 uptake of the reduced Na-added Cu-NaZSM-5 zeolite at comparatively lower temperature seems to cause the oxidation activity to be generated at lower temperature as indicated by the TPO in the presence of O_2.

Conclusions

Alkali-metal added to Cu-NaZSM-5 zeolite was confirmed to promote the gas-phase catalytic oxidation of benzyl alcohol, particularly the activity of the partial oxidation, even at lower reaction temperature. The state and the role of the alkali metal added to the Cu-NaZSM-5 zeolite catalysts in the catalytic oxidation of benzyl alcohol were studied using various physicochemical measurements including CO and ethanol adsorptions, TPD and TPO of ethanol, TPR of the catalysts, O_2 uptake of the reduced catalysts and XPS of the catalysts, in addition to the results of the gas-phase catalytic oxidation of benzyl alcohol. The alkali-metal in Cu-NaZSM-5 zeolite was confirmed to be present as an oxide such as Na_2O by DTA-GA analysis, in addition to consideration of the calcination conditions of the alkali-metal-added Cu-NaZSM-5 zeolites. On the basis of XPS observations, the added alkali metal was suggested to be located in the neighbourhood of the Cu species, as a ligand, rather than being covered by the Cu species. One of the roles of the added alkali metal is to help accommodate the adsorbed oxygen species, which is dissociated and responsible for the partial oxidation of benzyl alcohol. Also, the alkali metal may help the reactant alcohol to be adsorbed more strongly on the catalyst and to be oxidized to the corresponding aldehyde as supported by the comparison of both TPD spectra of ethanol on Na-added Cu-NaZSM-5 and Cu-NaZSM-5 zeolites. TPO of ethanol indicated that the Cu ion reduced during the benzyl alcohol oxidation can be more easily re-oxidized in the alkali-metal-added Cu-NaZSM-5 zeolite. Thus the added alkali metal was considered to promote the re-oxidation step of Cu^{I} to Cu^{II} in Cu-NaZSM-5 zeolite.

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