# Catalytic activity of NaZSM-5 supported Cu catalysts with or without added alkali metal in benzyl alcohol oxidation

#### Souichi Sueto, Satoru Nishiyama, Shigeru Tsuruya\* and Mitsuo Masai†

Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Nada, Kobe 657 Japan

ssue

Published on 01 January 1997. Downloaded on 24/10/2014 08:13:07.

The vapour-phase catalytic oxidation of benzyl alcohol has been carried out over NaZSM-5 supported copper and alkali-metaladded NaZSM-5 supported Cu catalysts. The NaZSM-5 zeolite supported copper catalyst has been prepared by three different methods, impregnation (Cu<sub>imp1</sub>/NaZSM-5), modified impregnation (Cu<sub>imp2</sub>/NaZSM-5) and also ion-exchange (Cu<sub>ex</sub>-NaZSM-5) methods. The preparation method of the NaZSM-5 supported Cu catalyst influenced the oxidation activity of the catalysts, regardless of the alkali-metal addition. The NaZSM-5 supported copper catalyst (Cu<sub>imp1</sub>/NaZSm-5) prepared by the impregnation method was found to show the highest oxidation activity among the prepared catalysts. Addition of alkali-metal to the NaZSM-5 supported Cu catalysts prepared by the different methods enhanced the oxidation activity, particularly the partial oxidation activity of the Cu-NaZSM-5 catalysts. The Na ions originally present in the NaZSM-5 support which maintain the charge neutrality were found not to affect substantially the catalytic activity. The redox behaviour and the structure of the Cu species anchored in the NaZSM-5 support were investigated using O<sub>2</sub> uptake, CO adsorption and XRD measurements. The interaction of the Cu species impregnated in the NaZSM-5 zeolite with O<sub>2</sub> was promoted by adding alkali metals. The alkali metals added to the Cu<sub>imp</sub>/NaZSM-5 zeolites were suggested to enhance the formation of the oxidic Cu species, which are considered to be responsible for the oxidation activity.

Because Cu ions are well known to show redox properties, a variety of homogeneous Cu complexes have been reported<sup>1</sup> to show catalytic behaviour for liquid-phase oxidation. Cu species anchored on supports such as oxides have also been studied as catalysts for gas-phase catalytic reactions incorporating a redox cycle.<sup>2,3</sup> Among supported Cu catalysts, interest has been focused on Cu ion-exchanged ZSM-5 zeolite as an effective catalyst for catalytic NO<sub>x</sub> decomposition.<sup>4-7</sup> The oxidative coupling polymerization of 2,6-dimethylphenol to the corresponding polyphenylene oxide, an important engineering plastic, using a Cu-pyridine complex as the catalyst discovered by Hay et al.8,9 has been one of the most successful industrial utilizations of a homogeneous Cu complex. We have previously reported<sup>10</sup> that alkali-metal addition to the Cu-pyridine complex caused an increase in the catalytic activity for the oxidative coupling reaction of 2,6-dimethylphenol. A Cu-alkali (basic copper) system in the absence of an organic base such as pyridine has been reported<sup>11-13</sup> to show effective catalytic activity for the oxidative coupling reaction of 2,6-dimethylphenol. We have also reported  $^{14-16}$  the effect of alkali-metal addition to Cu ion-exchanged NaZSM-5 zeolite catalyst in the gas-phase catalytic oxidation of benzyl alcohol. The added alkali metals were found<sup>14-16</sup> to be effective promoters for the oxidation of benzyl alcohol, particularly partial oxidation to form benzaldehyde. Cu-supported silica catalysts prepared by an impregnation method have been found<sup>17</sup> to show higher catalytic activity for benzyl alcohol oxidation than the corresponding Cu catalyst prepared by ion-exchange.

In this study, we have investigated the catalytic activity for benzyl alcohol oxidation of the Cu-supported NaZSM-5 catalyst prepared by the two different impregnation methods to compare the catalytic activity of the Cu ion-exchanged NaZSM-5 zeolite reported previously. The influence of the method of supporting Cu on the NaZSM-5 zeolite, the supported amount of Cu, and the alkali metal added to the Cu supported NaZSM-5 zeolites prepared by different methods on the catalytic activity of benzyl alcohol oxidation were examined in connection with the difference in the structure and the redox properties of the supported Cu species.

#### Experimental

#### **Catalyst preparation**

NaZSM-5 zeolite (Si/Al atomic ratio, 40) was synthesized by a method similar to that previously reported.<sup>18-20</sup> The Cusupported NaZSM-5 catalysts were prepared by the following three methods: (A) Cu-supported NaZSM-5 catalyst (Cu<sub>imp1</sub>/NaZSM-5) prepared by impregnation method: after the NaZSM-5 zeolite was immersed in ca. 5 cm<sup>3</sup> of an aqueous solution of а prescribed amount of  $Cu(CH_3COO)_2 \cdot H_2O$ , the Cu salt was quickly impregnated in the NaZSM-5 zeolite by evaporating the solvent within about 5 min. The  $\mathrm{Cu}_{\mathrm{imp1}}/\mathrm{NaZSM}\text{-}5$  was dried at 393 K overnight and calcined at 773 K for 3 h in flowing air. (B) Cu-supported NaZSM-5 catalyst (Cu<sub>imp2</sub>/NaZSM-5) prepared by an impregnation method: the synthesized NaZSM-5 zeolite was immersed in 100 cm<sup>3</sup> of an aqueous solution of a prescribed amount of  $Cu(CH_3COO)_2 \cdot H_2O$  for ca. 2 h. After standing for 2 h, the solvent was gradually evaporated within about 40 min. The Cu<sub>imp2</sub>/NaZSM-5 zeolite was dried at 393 K overnight and calcined at 773 K for 3 h in flowing air. (C) Cu supported NaZSM-5 catalyst (Cuex-NaZSM-5) prepared by an ion-exchange method: NaZSM-5 zeolite was ionexchanged using 100 cm<sup>3</sup> of an aqueous solution containing a dissolved prescribed amount of  $Cu(CH_3COO)_2 \cdot H_2O$ . After filtration of the resulting Cu ion-exchanged NaZSM-5 zeolite, the Cu<sub>ex</sub>-NaZSM-5 was dried at 393 K overnight and calcined at 773 K for 3 h in flowing air.

Alkali-metal Cu-supported NaZSM-5 zeolites were prepared by impregnating a prescribed amount of alkali-metal acetate into each NaZSM-5 supported Cu catalyst followed by drying at 393 K overnight and calcination at 773 K for 3 h in flowing air.

<sup>&</sup>lt;sup>†</sup> Present address: Department of Applied Physics and Chemistry, The Fukui University of Technology, Gakuen 3-6-1, Fukui, 910 Japan.

#### Gas-phase catalytic oxidation of benzyl alcohol

The gas-phase catalytic oxidation was performed in a conventional fixed-bed type vertical microreactor under a continuous gas flow at atmospheric pressure. Further details for the reaction procedure and the analyses of the reaction products are given elsewhere.<sup>16</sup> The main oxidation products were benzaldehyde and carbon dioxide. The conversion of benzyl alcohol and the yields of both benzaldehyde and carbon dioxide were calculated as previously.<sup>16</sup> The carbon balances before and after the catalytic oxidation of benzyl alcohol were 80-100%, usually >90%.

### Thermal gravimetry (TG)-differential thermal analysis (DTA) measurement of the carbonaceous material produced

Carbonaceous material (coke) accumulated on the catalyst during the benzyl alcohol oxidation was oxidized using DTA-TG apparatus (Shimazu Model DTG-40) into which a controlled mixed gas of  $O_2$  and  $N_2$  can be introduced. The rate of temperature increase was 20 K min<sup>-1</sup>.

#### Measurement of O<sub>2</sub> uptake

The amount of  $O_2$  uptake of the pre-reduced catalysts was measured using conventional semi-micro gas adsorption equipment made of a capillary-glass tube to make the dead volume as small as possible. Details of the procedure are given elsewhere.<sup>16</sup>

#### Measurement of CO adsorption

The amount of CO adsorption was measured using the semimicro gas adsorption equipment used for the measurement of  $O_2$  uptake. Details of the procedure are given elsewhere.<sup>16</sup>

### Measurement of X-ray diffraction (XRD) pattern of K-Cu-supported NaZSM-5 catalysts

The powder XRD patterns of the catalyst samples were measured at room temperature using Rigaku XRD equipment with Cu-K $\alpha$  radiation as the X-ray source.

#### Results

#### Gas-phase catalytic oxidation of benzyl alcohol

The oxidation of benzyl alcohol was performed using alkalimetal–Cu (1.0 wt.%) supported NaZSM-5 [Cu(1)<sub>imp1</sub>/NaZSM-5] zeolites (Table 1). The Cu species prepared by impregnation method 1, as well as by the ionexchange method reported previously,<sup>14–16</sup> was found to show catalytic activity for benzyl alcohol oxidation as evidenced from the comparison between NaZSM-5 and

Table 1 The effect of added alkali metal on the benzyl alcohol oxidation catalysed by  $M-Cu_{imp1}/Na-ZSM-5$  (Si/Al = 40) zeolites<sup>a</sup> (M = alkali metal)

catalyst	benzaldehyde yield (%)	CO <sub>2</sub> yield (%)
NaZSM-5	0.4	trace
Na-NaZSM-5	0.4	trace
Cu <sub>imp1</sub> /NaZSM-5	1.8	0.2
Li–Cu <sub>imp1</sub> /NaZSM-5	2.9	0.2
Na-Cu <sub>ima</sub> /NaZSM-5	3.8	0.2
$K-Cu_{imp1}/NaZSM-5$	7.2	0.5
Rb-Cu <sub>imp1</sub> /NaZSM-5	5.7	0.4
Cs-Cu <sub>imp1</sub> /NaZSM-5	4.7	0.4

<sup>a</sup> Catalyst, 0.5 g, Cu = 1.0 wt.%, added M/Cu atomic ratio = 1, Si/Al atomic ratio = 40; reaction temperature, 573 K; W/F = 21.7 g cat. min mol<sup>-1</sup>; partial pressure of N<sub>2</sub> = 9.02 × 10<sup>4</sup> Pa; partial pressure of O<sub>2</sub> = 8.34 × 10<sup>3</sup> Pa; partial pressure of benzyl alcohol = 2.78 × 10<sup>3</sup> Pa.

Cu(1)<sub>imp1</sub>/NaZSM-5 catalysts. The oxidation activity increased on adding alkali metal to the Cu<sub>imp1</sub>/NaZSM-5 zeolite, regardless of the alkali metal. The Na [the amount of the added Na was the same as that added to the Cu(1)<sub>imp1</sub>/NaZSM-5 zeolite] added to the NaZSM-5 zeolite did not promote the catalytic activity (Table 1). Addition of alkali metals to the Cu(1)<sub>imp1</sub>/NaZSM-5 catalysts was found to inhibit the deactivation of the initial oxidation activity based on a comparison with the relationship between the conversion and time on-stream over the Cu<sub>imp1</sub>/NaZSM-5 catalysts with or without added alkali metal.

Increase in the reaction temperature led to an increase in the yields of benzaldehyde and carbon dioxide in both Cu(1)<sub>imp2</sub>/NaZSM-5 and K(4)–Cu(1)<sub>imp2</sub>/NaZSM-5 (K/Cu = 4) (Fig. 1). The yield of benzaldehyde catalysed by K(4)–Cu(1)<sub>imp2</sub>/NaZSM-5 zeolite increased significantly with increased reaction temperature, in contrast to the yield of carbon dioxide which showed only a gradual increase.

The yield of benzaldehyde catalysed by the Cu<sub>imp1</sub>/NaZSM-5 zeolite increased with an increase in the amount of Cu added up to ca. 1 wt.% Cu but then decreased at higher loadings [Fig. 2(a)]. Yet a further increase in the amount of the impregnated Cu did not lead to a large increase in the yield of benzaldehyde [Fig. 2(a)]. The yield of carbon dioxide catalysed by the Cu<sub>imp1</sub>/NaZSM-5 zeolite relative to the amount of supported Cu was appreciably lower than the yield of benzaldehyde. The K(4)–Cu<sub>imp1</sub>/NaZSM-5 zeolite showed considerably higher oxidation activity than the Cu<sub>imp1</sub>/NaZSM-5 zeolite with no potassium [Fig. 2(b)]. The yield of benzaldehyde catalysed by the K(4)–Cu\_{imp1}/NaZSM-5 zeolite sharply increased with an increase in the amount of supported Cu up to ca. 1 wt.% Cu. Adding potassium to the Cu<sub>imp1</sub>/NaZSM-5 zeolite was thus confirmed to promote selectively partial oxidation activity with benzaldehyde formation.

The yield of benzaldehyde catalysed by  $Cu_{imp2}/NaZSM-5$  zeolite increased with an increase in the amount of impregnated Cu up to *ca*. 0.5 wt.%, but a further increase in Cu led essentially to a plateau in the yield of benzaldehyde [Fig. 3(a)]. The yield of benzaldehyde catalysed by K(1)–Cu<sub>imp2</sub>/NaZSM-5 zeolite also sharply increased with an initial increase in the amount of supported Cu and increased to a lesser degree with a further increase in the supported Cu [Fig. 3(b)]. Yields of carbon dioxide catalysed by both catalysts were very low and scarcely increased with Cu loading.

The yield of benzaldehyde increased with an increase in the added alkali metal/Cu (alkali metal = Na or K) atomic ratio



**Fig. 1** Effect of reaction temperature on the yields in the benzyl alcohol oxidation. Catalyst, 0.5 g; catalyst mass/flow rate (W/F) = 21.7 g cat. min mol<sup>-1</sup>;  $P_{N_2} = 9.02 \times 10^4$  Pa;  $P_{O_2} = 8.34 \times 10^3$  Pa;  $P_{BOH} = 2.78 \times 10^3$  Pa; ( $\bullet$ ,  $\blacksquare$ ), K-Cu(1)<sub>imp2</sub>/NaZSM-5 (Si/Al = 40) catalyst; (O,  $\Box$ ), Cu(1)<sub>imp2</sub>/NaZSM-5 (Si/Al = 40) catalyst; ( $\bullet$ ,  $\bigcirc$ ), benzaldehyde yield; ( $\blacksquare$ ,  $\Box$ ), CO<sub>2</sub> yield.



**Fig. 2** (a) Influence of Cu loading on the yields using  $Cu_{imp1}/NaZSM-5$  (Si/Al = 40) catalyst. Reaction temperature, 573 K; other conditions as in Fig. 1; ( $\bullet$ ), benzaldehyde; ( $\bigcirc$ ), CO<sub>2</sub>. (b) Influence of Cu loading on the yields using K(1)–Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) catalyst. Conditions as in (a); ( $\bullet$ ), benzaldehyde; ( $\bigcirc$ ), CO<sub>2</sub>.

for the alkali-metal–Cu<sub>imp1</sub>/NaZSM-5 catalysts, passed through a maximum value at the atomic ratio of *ca.* 1, and decreased upon further increase of added alkali metal/Cu atomic ratio, regardless of the alkali metal [Fig. 4(a), (b)]. Yields of CO<sub>2</sub> were very low and hardly varied with an increase in the atomic ratio.

The effect of the amount of K added to the  $Cu(1)_{imp2}/NaZSM-5$  zeolite on the oxidation activity is illustrated in Fig. 5. An increase in the K/Cu atomic ratio caused an increase in the yield of benzaldehyde and produced a maximum value for the benzaldehyde yield at a K/Cu atomic ratio of *ca*. 4.

Fig. 6 shows the effect of the added Na/Cu atomic ratio on the oxidation activity for benzyl alcohol using Na–Cu(1)<sub>ex</sub>–NaZSM-5 zeolite as the catalyst. The yield of benzaldehyde showed a maximum value at an added Na/Cu atomic ratio of *ca.* 4, as observed using K–Cu(1)<sub>imp2</sub>/NaZSM-5 catalyst (Fig. 5).

# Carbonaceous materials accumulated on the used Cu<sub>imp1</sub>/NaZSM-5 and K-Cu<sub>imp1</sub>/NaZSM-5 catalysts

Carbonaceous materials (coke) accumulated on both the used  $Cu(1)_{imp1}/NaZSM-5$  and  $K(1)-Cu(1)_{imp1}/NaZSM-5$  catalysts, which were used over a process time of 4 h (reaction conditions as in Table 1), were observed by differential thermal analysis (DTA)-thermogravimetry (TG). The temperature programmed oxidation (TPO) spectra obtained by DTA-TG are illustrated in Fig. 7. The amount of coke accumulated on the Cu(1)<sub>imp1</sub>/NaZSM-5 and K(1)-Cu(1)<sub>imp1</sub>/NaZSM-5 catalysts was 1.70 and 1.25 mg, respectively, based on the TG



**Fig. 3** (a) Influence of Cu loading on the yields using  $Cu_{imp2}/NaZSM-5$  (Si/Al = 40) catalyst. Conditions as in Fig. 2; ( $\bullet$ ), benzaldehyde; ( $\bigcirc$ ), CO<sub>2</sub>. (b) Influence of Cu loading on the yields using K(1)-Cu(1)<sub>imp2</sub>/NaZSM-5 (Si/Al = 40) catalyst. Conditions as in (a); ( $\bullet$ ), benzaldehyde; ( $\bigcirc$ ), CO<sub>2</sub>.

results. Thus the addition of alkali metal to the  $Cu_{imp1}/NaZSM-5$  zeolite caused the formation of carbonaceous material on the zeolite to decrease appreciably, in agreement with the reactivity in which the deactivation was largely inhibited over the K- $Cu_{imp1}/NaZSM-5$  zeolite catalyst. A sharp peak at 573 K and a broad peak having a maximum at *ca*. 673 K, and a sharp peak at 673 K were observed in the DTA spectra of the used  $Cu(1)_{imp1}/NaZSM-5$  and used  $K(1)-Cu(1)_{imp1}/NaZSM-5$  zeolites (Fig. 7). These exothermic DTA peaks are considered to be due to the oxidation of carbonaceous materials accumulated on the samples.

## $O_2$ uptake of pre-reduced $Cu_{imp}/NaZSM-5$ and the alkalimetal– $Cu_{imp}/NaZSM-5$ zeolites

The amounts of O<sub>2</sub> uptake of the Cu<sub>imp</sub>/NaZSM-5 and the alkali-metal–Cu<sub>imp</sub>/NaZSM-5 zeolites were measured after reducing both the Cu supported NaZSM-5 zeolites by evacuation at 773 K and treatment with CO at 773 K (Table 2). The added alkali metal/Cu atomic ratios of the Cu supported NaZSM-5 zeolites prepared by impregnation methods (A) and (B) were 1 and 4, respectively, since the alkali metal–Cu<sub>imp1</sub>/NaZSM-5 and alkali metal–Cu<sub>imp2</sub>/NaZSM-5 zeolites showed maximum activities at these ratios, as illustrated in Fig. 4(b) and 5. The amounts of O<sub>2</sub> uptake of the alkali-metal–Cu supported NaZSM-5 zeolites which were prereduced were found to be greater than those of the corresponding Cu-supported zeolites without added alkali metal. The amounts of O<sub>2</sub> uptake of the pre-reduced alkali-metal–Cu<sub>imp1</sub>/NaZSM-5 zeolites were found to be greater than those of the corresponding Cu-supported zeolites without added alkali metal.



**Fig. 4** (a) Influence of added Na/Cu atomic ratio on the yields using Na–Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) catalyst. Conditions as in Fig. 2; ( $\bullet$ ), benzaldehyde; ( $\bigcirc$ ), CO<sub>2</sub>. (b) Influence of added K/Cu atomic ratio on the yields using K–Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) catalyst. Conditions as in (a); ( $\bullet$ ), benzaldehyde; ( $\bigcirc$ ), CO<sub>2</sub>.

than those of the pre-reduced alkali metal– $Cu_{imp2}$ /NaZSM-5 zeolites, irrespective of the particular added alkali metal.

#### CO adsorption of Cu<sub>imp2</sub>/NaZSM-5 and alkalimetal-Cu<sub>imp2</sub>/NaZSM-5 zeolites

The amounts of CO adsorbed on the  $Cu_{imp2}/NaZSM-5$  and alkali-metal- $Cu_{imp2}/NaZSM-5$  zeolites, which were evacuated



**Fig. 5** Influence of added K/Cu atomic ratio on the yield using K-Cu(1)<sub>imp2</sub>/NaZSM-5 (Si/Al = 40) catalyst. Conditions as in Fig. 2; ( $\bullet$ ), benzaldehyde; ( $\bigcirc$ ), CO<sub>2</sub>.



**Fig. 6** Influence of added Na/Cu atomic ratio on the yield using Na-Cu(1)<sub>ex</sub>-NaZSM-5 (Si/Al = 40) catalyst. Conditions as in Fig. 2; ( $\bullet$ ), benzaldehyde; ( $\bigcirc$ ), CO<sub>2</sub>.

at 773 K for 2 h, were measured at room temperature. The amount of CO adsorption of the Cu(1)<sub>imp2</sub>/NaZSM-5 zeolite was  $8.1 \times 10^{-6}$  mol (g cat.)<sup>-1</sup> In contrast, all the alkali-metal–Cu(1)<sub>imp2</sub>/NaZSM-5 zeolites (alkali metal = Na, K, Rb or Cs;



Fig. 7 DTA-TG spectra of used Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) and used K(1)-Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40). Rate of temperature increase, 20 K min<sup>-1</sup>;  $O_2$ -N<sub>2</sub> (1/4) (30 cm<sup>3</sup> min<sup>-1</sup>); a, TGA spectrum of used Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) catalyst; b, DTA spectrum of used Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) catalyst; d, DTA spectrum of used K(1)-Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) catalyst; d, DTA spectrum of used K(1)-Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) catalyst; d, DTA spectrum of used K(1)-Cu(1)<sub>imp1</sub>/NaZSM-5 (Si/Al = 40) catalyst.

Table 2  $O_2$  uptake of Cu supported NaZSM-5 (Si/Al = 40) zeolites with and without alkali metal<sup>4</sup>

	Amount of $O_2$ uptake $10^6 \text{ mol (g-cat)}^{-1}$	
catalyst	impregnation method 1	2
Cu(1) <sub>imp</sub> /NaZSM-5	23.4	23.6
Li-Cu(1) <sub>imp</sub> /NaZSM-5	26.8	24.2
Na-Cu(1) <sub>imp</sub> /NaZSM-5	27.5	24.2
K-Cu(1) <sub>imp</sub> /NaZSM-5	33.8	30.3
Cs-Cu(1) <sub>imp</sub> /NaZSM-5	27.3	27.1
Rb-Cu(1) <sub>imp</sub> /NaZSM-5	27.5	26.3

<sup>*a*</sup> Impregnation method 1, added alkali metal/Cu (atomic ratio) = 1; impregnation method 2, added alkali-metal/Cu (atomic ratio) = 4.

alkali metal/Cu = 4) evacuated at 773 K for 2 h, did not adsorb CO.

#### **XRD** patterns of catalyst

The XRD patterns of both the K–Cu(1)<sub>imp1</sub>/NaZSM-5 and K–Cu(1)<sub>imp2</sub>/NaZSM-5 zeolites, which were pretreated at 773 K for 2 h in flowing air were observed with variation in the added K/Cu atomic ratio between 1 and 6 (Fig. 8). The XRD peaks of CuO were observed at  $2\theta = 35.4$  and  $38.5^{\circ}$ , respectively, although they were rather broad and ambiguous. The



**Fig. 8** (a) XRD patterns of K-added  $Cu_{imp1}/NaZSM-5$  (Si/Al = 40): (1) NaZSM-5, (2) K/Cu = 0, (3) K/Cu = 1, (4) K/Cu = 4, (5) K/Cu = 6. (b) XRD pattern of K-Cu<sub>imp2</sub>/NaZSM-5 (Si/Al = 40) catalysts. (1) NaZSM-5, (2) K/Cu = 0, (3) K/Cu = 2, (4) K/Cu = 4, (5) K/Cu = 6.

CuO peaks of K(1)–Cu(1)<sub>imp1</sub>/NaZSM-5 [Fig. 8(a) (3)] tended to become larger than that of the Cu(1)<sub>imp1</sub>/NaZSM-5 without K [Fig. 8(a) (2)]. However, further addition of K to the Cu(1)<sub>imp1</sub>/NaZSM-5 zeolite tended to decrease the intensity of the CuO peaks. The CuO peaks of K(6)–Cu(1)<sub>imp1</sub>/NaZSM-5 almost disappeared as illustrated in Fig. 8(*a*) (5). The CuO peaks, which were observed in the Cu(1)<sub>imp1</sub>/NaZSM-5, were hardly observed in the XRD pattern of the Cu(1)<sub>imp2</sub>/NaZSM-5 zeolite [Fig. 8(b) (2)] and were very similar to that of the NaZSM-5 zeolite [Fig. 8(b) (1)]. The addition of K to the Cu(1)<sub>imp2</sub>/NaZSM-5 zeolite produced broad CuO peaks in the XRD patterns [Fig. 8(b) (3, 4)]. However, too much added K again tended to diminish the intensities of the CuO peaks in the XRD of the Cu(1)<sub>imp2</sub>/NaZSM-5 zeolite [Fig. 8(*b*) (5)].

#### Discussion

Comparison of the catalytic activity of both the  $K-Cu(1)_{imp2}/NaZSM-5$  (Fig. 5) and  $Na-Cu(1)_{ex}-NaZSM-5$  (Fig. 6) zeolites showed that the maximum yields of benzaldehyde over both catalytic systems were obtained at an added alkali metal/Cu atomic ratio of *ca.* 4, in spite of the results in which the Cu(1)<sub>imp2</sub>-NaZSM-5 catalyst originally includes 2 equivalents more Na ions relative to the supported Cu than the Cu(1)<sub>ex</sub>/NaZSM-5 catalyst. This result suggests that the Na ions originally present in the NaZSM-5 support (to maintain charge neutrality) are considered not to substantially affect the catalytic activity of benzyl alcohol oxidation, in contrast to the added Na ions.

We have previously reported<sup>17</sup> that a Cu/SiO<sub>2</sub> catalyst  $(Cu_{imp}/SiO_2)$  prepared by impregnation was found to have a higher catalytic activity for the oxidation of benzyl alcohol than the corresponding one prepared by an ion-exchange method, irrespective of the presence of the added alkali metal. In the present study, Cu<sub>imp1</sub>/NaZSM-5 zeolite had a higher catalytic activity than  $Cu_{imp2}/NaZSM-5$  zeolite [the yields (%) of benzaldehyde over  $Cu(1)_{imp1}/NaZSM-5$ and Cu(1)imp2/NaZSM-5 zeolite catalysts without added alkali metal were as follows: 2.0 and 1.1 at 573 K, 8.1 and 2.5 at 603 K and 20.6 and 15.9 at 643 K, respectively]. Impregnation method B is similar to an ion-exchange method (or more properly an adsorption method) rather than a typical impregnation method owing to the long standing time in the Cu<sup>2</sup> solution with stirring followed by very slow evaporation of the solvent. The Cu<sub>imp1</sub>/NaZSM-5 zeolite will thus contain more aggregated Cu species, which are considered<sup>17</sup> to contribute to the catalytic activity for the benzyl alcohol oxidation, than the  $Cu_{imp2}/NaZSM-5$  zeolite, on which the Cu species may be more isolated as ion-exchanged Cu species. The yield of benzaldehyde was at a maximum at a Cu wt.% of ca. 1 [Fig. 2(a)]. The catalytically active oxidic Cu species may thus have an optimum size, rather than isolated Cu species or bulk particulate Cu species. Since the XRD peaks identified as CuO are very broad and rather ambiguous, the sizes of the oxidic Cu species are probably fairly small. The intensities of XRD peaks at  $2\theta$  35.4 and 38.5°, identified as CuO species appear to increase with K/Cu atomic ratios of ca. 1 and 4 for K-Cu<sub>imp1</sub>/NaZSM-5 and K-Cu<sub>imp2</sub>/NaZSM-5 zeolites, respectively (Fig. 8). On the other hand, the yields of benz- $K-Cu_{imp1}/NaZSM-5$ aldehyde catalysed by and K-Cu<sub>imp2</sub>/NaZSM-5 zeolites were also found to have maximum values at added K/Cu atomic ratios of ca. 1 and 4, respectively [Figs. 4(b), 5]. Thus, the small oxidic Cu species seem to have a correlation with the activity of the partial oxidation, and the added alkali metal may play an important role in formation of the active oxidic Cu species.

No CO adsorption was observed on the alkalimetal- $Cu_{imp2}$ /NaZSM-5 zeolites which were pre-reduced, differing from the corresponding  $Cu_{imp2}$ /NaZSM-5 zeolites which showed CO adsorption, indicating that the added alkali metal promotes the formation of Cu<sup>2+</sup> species, such as oxidic Cu species. The amounts of O2 uptake by both the alkalimetal-Cu\_{imp1}/NaZSM-5 and Cu\_{imp2}/NaZSM-5 zeolites prereduced by CO treatment at high temperature were found to be higher than the corresponding counterparts without the added alkali metal (Table 2). The larger affinity for oxygen of alkali-metal–Cu $_{imp1}$ /NaZSM-5 supports the ease of the formation of the active oxidic Cu species by addition of alkali metal. The increase in the amount of O<sub>2</sub> uptake upon adding alkali metal has been reported for Cu ion-exchanged NaZSM-5 zeolite and this also led to Cuex-NaZSM-5 zeolite with an increase in the charge of the Cu species as revealed by the ease of the interaction of oxygen molecules and the dissociation of adsorbed oxygen molecules.14-16 The added alkali metals may render the formation of oxo Cu cation species<sup>21</sup> (Cu-O-Cu)<sup>2+</sup> more facile, in addition to oxidic Cu species, in the Cu supported NaZSM-5 zeolites; oxo Cu cations may also have higher catalytic activity for partial oxidation.

It is believed that the active species for partial oxidation are small oxidic Cu species, rather than isolated Cu ions or bulk particles of CuO, and the added alkali metal may play an important role to produce such active oxidic Cu species, through dissociation of adsorbed oxygen molecules. The active Cu species will be located in the pores of NaZSM-5 zeolites, although the possibility that some of the oxidic Cu species formed upon adding alkali metal are on the outer surface of the zeolite cannot be ruled out.

#### Conclusions

Cu<sub>imp1</sub>/NaZSM-5 zeolite, in which the Cu species were impregnated over a short time (about 5 min), was found to have a different catalytic behaviour for benzyl alcohol oxidation, particularly at lower Cu contents, from that of Cu<sub>imp2</sub>/NaZSM-5 zeolite, of which the Cu species was slowly impregnated over ca. 40 min after immersion for ca. 2 h. Addition of alkali metals to both the  $Cu_{imp1}/NaZSM-5$  and Cu<sub>imp2</sub>/NaZSM-5 zeolites caused an increase in the partial oxidation activity of benzyl alcohol oxidation. The Na originally present in the NaZSM-5 zeolite (to maintain charge neutrality) did not promote partial oxidation activity, in contrast to alkali metals added by impregnation. The oxidation activities of K-Cu<sub>imp1</sub>/NaZSM-5 and K-Cu<sub>imp2</sub>/NaZSM-5 zeolites were found to show maximum activities at added K/Cu atomic ratios of ca. 1 and 4 respectively. The added alkali metal increased the amount of O2 adsorption on prereduced  $Cu_{imp1}/NaZSM-5$  and  $Cu_{imp2}/NaZSM-5$  zeolites. No CO was adsorbed on the M-Cu $_{imp2}$ /NaZSM-5 evacuated at 773 K. Oxidic Cu species, rather than isolated Cu ions or bulk particles of CuO, are suggested to be responsible for catalysing the oxidation of benzyl alcohol, particularly partial oxidation.

The authors thank Mr Kenji Nomura of Kobe University for his technical assistance.

#### References

- 1 S. Tsuruya, Trends Inorg. Chem., 1993, 3, 71.
- 2 Y. Ben Taarit and M. Che, in *Catalysis by Zeolites*, ed. C. Naccache, Y. Ben Taarit, J. C. Vedrine, G. Coudurier and H. Praliaud, Elsevier, Amsterdam, 1980, p. 167.
- 3 C. Naccache and Y. Ben Taarit, in Zeolites: Science and Technology, ed. F. R. Ribeiro, A. E. Rodrigues, L. D. Rollmann and C. Naccache, Martinus Nijhoff, The Hague, 1984, p. 379.
- 4 M. Iwamoto, M. Yokoo, K. Sakai and S. Kagawa, J. Chem. Soc., Faraday Trans. 1, 1981, 77, 1629.
- 5 M. Iwamoto, H. Yahiro, K. Tanda, Y. Mizuno, Y. Mine and S. Kagawa, J. Phys. Chem., 1991, 95, 3727.
- 6 M. Iwamoto, H. Yahiro, N. Mizuno, W-X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, J. Phys. Chem., 1992, 96, 9360.
- 7 M. Iwamoto, N. Mizuno and H. Yahiro, Proceedings of 10th International Congress on Catalysis, ed. L. Guczi, F. Solymosi and P. Tetenyi, Academicai Kiado, Budapest, 1993, p. 213.
- 8 A. S. Hay, H. S. Blanchard, G. F. Endres and J. W. Eustance, J. Am. Chem. Soc., 1959, 81, 6335.
- 9 A. S. Hay, Polym. Eng. Sci., 1976, 16, 1.
- 10 S. Tsuruya, T. Shirai, T. Kawamura and T. Yonezawa, Makromol. Chem., 1970, 132, 57.
- 11 S. Tsuruya, K. Nakamae and T. Yonezawa, J. Catal., 1976, 44, 40.
- 12 S. Tsuruya, T. Takaki, M. Masai, J. Catal., 1984, 89, 511.
- 13 T. Takaki, S. Nishiyama, S. Tsuruya and M. Masai, Proceedings of World Congress III of Chemical Engineering, The Society of Chemical Engineers, Japan, Tokyo, 1986, vol. IV, p. 330.
- 14 H. Hayashibara, T. Nanbu, S. Nishiyama, S. Tsuruya and M. Masai, in *Proceedings, 9th International Zeolite Conference, Montreal*, ed. R. von Ballmoos, J. B. Higgins and M. M. J. Treaty, Butterworth-Heinemann, London, 1993, p. 575.
- 15 H. Hayashibara, S. Nishiyama, S. Tsuruya and M. Masai, J. Catal., 1995, 153, 254.
- 16 M. Genta, S. Nishiyama, S. Tsuruya and M. Masai, J. Chem. Soc., Faraday Trans., 1996, 92, 1267.
- 17 M. Arai, S. Nishiyama, S. Tsuruya and M. Masai, J. Chem. Soc., Faraday Trans., 1996, 92, 2631.
- 18 N. Y. Chen, S. J. Lucki and W. E. Garwood, US Pat. 3,700,585, 1972.
- 19 M. Nakao, S. Nishiyama, S. Tsuruya and M. Masai, Inorg. Chem., 1992, 31, 4662.
- 20 Y. Itho, S. Nishiyama, S. Tsuruya and M. Masai, J. Phys. Chem., 1994, 98, 960.
- 21 T. Beutel, J. Sarkany, G-D. Lei, J. Y. Yan and W. H. M. Sachtler, J. Phys. Chem., 1996, 100, 845.

Paper 6/06974F; Received 11th October, 1996