

Promoted partial oxidation activity of alkali metal added-Co catalysts supported on NaY and NaUSY zeolites in the gas-phase catalytic oxidation of benzyl alcohol

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Abstract

A study on the oxidation activity of cobalt (Co) catalysts ion-exchanged and impregnated on NaY and NaUSY (ultra stable Y) zeolites and their alkali metal added counterpart, and the nature of the active supported Co species was carried out using the gas-phase catalytic oxidation of benzyl alcohol. The main oxidation products over the supported Co catalysts used in this study were benzaldehyde and CO₂. The partial oxidation activity increased with increasing the amount of Co in the Co catalyst (Co/NaUSY_{imp}) impregnated on NaUSY zeolite, although the degree of the increase in the benzaldehyde yield tended to decrease in the region of the higher amount of Co. The yield of benzaldehyde over the Co catalyst (Co/NaY_{imp}) impregnated on NaY zeolite had a maximum at a comparatively lower amount of Co. The addition of an alkali metal to the impregnated and ion-exchanged Co catalysts with a low amount of Co (1 wt.%) effectively promoted the partial oxidation activity. The redox property of the supported Co catalysts was investigated using UV–vis diffuse reflectance (DR) spectra. The role of the added alkali metal was inferred to be assistance for Co²⁺ to be oxidized to Co³⁺ to form Co₃O₄ [Co²⁺(Co³⁺)₂O₄] which was assumed to be active species for the partial oxidation of benzyl alcohol. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Cobalt (Co) catalysts supported on various zeolites have been reported to be active in hydrocarbon dehydrogenation [1], ammoxidation [2], and NO reduction [3–6]. Cobalt ion and/or its complexes have been known to have redox properties and have been used as a catalyst for liquid-phase oxidation of hydrocarbons and alcohol using gaseous oxygen as an oxidant [7,8]. No *stoichiometric* oxidation process of alcohols using environmentally high-loading oxidant will be permitted from an environmental preservation point of view. The liquid- and gas-phase *catalytic* oxidations of alcohols using gaseous oxygen as an oxidant have been highlighted. We previously reported [9] the gas-phase catalytic oxidation of benzyl alcohol to benzaldehyde over Co ion-exchanged NaY (Co-NaY_{ic}) catalyst using gaseous

oxygen as an oxidant. However, both the yield and selectivity of benzaldehyde over the Co-NaY_{ic} catalyst were considerably low. Recently, Ru/Al₂O₃ [10] and Pd/hydroxyapatite [11] have been reported to be very efficient catalysts for the liquid-phase oxidation of alcohols. The liquid-phase oxidation of alcohols over Fe³⁺/montmorillonite-K10 was reported using H₂O₂, an example of an environmentally friendly oxidant [12]. We recently found that an alkali metal added to Co catalysts supported on NaY, and NaX zeolites promoted the partial oxidation in the gas-phase catalytic oxidation of benzyl alcohol using gaseous oxygen as an oxidant [13,14]. A drawback is that the zeolite structure of the alkali metal added Co catalysts supported on zeolite are disrupted by increasing the amount of the added alkali metal; the structural disruption of the zeolite supports causes the decline in the partial oxidation activity.

In the extension of the study on the gas-phase catalytic oxidation of benzyl alcohol over an alkali metal added supported Co catalysts, at first we used NaUSY (ultra stable Y type zeolite) as a support of the supported Co catalysts. We expected that the

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stability of the zeolitic structure of the NaUSY zeolite and the catalytic performance of the Co catalyst supported on NaUSY zeolite would be superior to that of the counterpart supported on NaY. Then, to prevent the destruction of the zeolitic structure and also to save the amount of Co consumption, the Co catalysts supported on NaY zeolite with a low amount of Co were prepared and the effect of alkali metal added to the Co catalysts on the partial oxidation activity were investigated. The states and the redox behavior of the Co species supported on the zeolite were investigated by UV–vis DR spectra to investigate the role of added alkali metals.

2. Experimental

2.1. Catalysts

Y type zeolite (Si/Al atomic ratio = 2.8, Tosoh) and ultra stable Y zeolite (USY, Si/Al atomic ratio = 15, Zeolyst) were treated with 1 N NaNO₃ aqueous solution to obtain perfectly Na ion-exchanged NaY and NaUSY zeolites. Co ion-exchanged NaY and NaUSY (Co-NaY_{ie}, Co-NaUSY_{ie}) and Co impregnated NaY and NaUSY zeolites (Co-NaY_{imp}, Co-NaUSY_{imp}) were prepared by conventional ion-exchange and impregnation methods using an aqueous solution of Co(NO₃)₂·6H₂O (Nacali Tesque, guaranteed reagent). Both catalysts were dried at 393 K overnight and calcined at 773 K for 5 h in flowing air. Alkali metal added Co-NaY_{ie} and Co-NaY_{imp} catalysts (alkali metal/Co-NaY_{ie} and alkali metal/Co-NaY_{imp}) were prepared by impregnating alkali metal acetate (Nacali Tesque, guaranteed reagent) to the Co-NaY_{ie} and the Co-NaY_{imp} catalysts. Both the alkali metal/Co-NaY_{ie} and alkali metal/Co-NaY_{imp} catalysts were calcined at 773 K for 3 h in flowing air. To measure the amount of Co ion-exchanged quantitatively, the homogeneous solution, produced by adding 1–2 drops of hydrogen fluoride (Hashimoto Chemical Co., guaranteed reagent, 47%) to the Co-NaY_{ie} and the Co-NaUSY_{ie} zeolites, was transferred to an atomic absorption spectrometer (Shimadzu, Type AA-6200) for measurement. The prepared catalyst is hereafter labeled such as K(4)/Co(1)/NaY_{imp}: where added K/Co atomic ratio = 4; supported Co = 1 wt.%. The numbers into parentheses of K and Co mean the added K/Co atomic ratio and the amount of the supported Co expressed in wt.%, respectively.

2.2. Gas-phase catalytic reaction of benzyl alcohol

Benzyl alcohol (Nacali Tesque, guaranteed reagent) was used without further purification after confirming that no impurity was detected by gas chromatography (GC). O₂ and N₂ gases were used after being passed through a column filled with silica gel. The gas-phase catalytic reaction was carried out at atmospheric pressure using a conventional continuous flow fixed-bed pyrex-glass reactor (i.d. 15 mm) vertically located in an electric furnace. A catalyst (usually 0.2 g) placed in the reactor was pretreated at 773 K for 2 h in flowing air. The reaction was started by feeding benzyl alcohol through a micro-feeder to the reactor. Typical reaction conditions were as follows: W/F = 8.70 g-cat min/mol (W, catalyst weight [g-cat]; F, total mol flow rate

[mol/min]), W = 0.2 g, F = 0.023 mol/min, benzyl alcohol: O₂: N₂ = 1: 3: 32 (mole ratio), reaction temperature, 623 K. The liquid products and recovered benzyl alcohol, after collection using a refrigerant (diethyl malonate + liquid N₂) and adding 1 cm³ N,N-dimethylformamide as an internal standard, were analyzed by a GC (Shimadzu GC-8A) with a FID detector at 373–473 K (programmed rate, 20 K/min) under N₂ flow (20 cm³/min) using a 2 m glass column packed with 5% PEG HD on Uniport HP (60/80 mesh). A 1 cm³ sample of the gaseous products, which was sampled by a gas-syringe, was analyzed by an intermediate-cell method [15] using a GC (Shimadzu GC-8A) equipped with a thermal conductivity detector using two 1 m stainless columns packed with silica gel (60–80 mesh) and molecular sieves 5A (60–80 mesh) at 393 and 293 K, respectively, under a H₂ carrier (35 cm³/min). The conversion, the yield and the selectivity of each product were defined as follows [16]:

$$\text{yield of benzyl alcohol (\%)} = \frac{[\text{benzaldehyde}]}{[\text{benzylalcohol}]} \times 100$$

$$\text{yield of CO}_2(\%) = \frac{\frac{1}{7}[\text{CO}_2]}{[\text{benzylalcohol}]} \times 100$$

$$\begin{aligned} \text{selectivity of benzaldehyde (\%)} \\ = \frac{[\text{benzaldehyde}]}{[\text{benzaldehyde}] + \frac{1}{7}[\text{CO}_2]} \times 100 \end{aligned}$$

$$\text{selectivity of CO}_2(\%) = \frac{\frac{1}{7}[\text{CO}_2]}{[\text{benzaldehyde}] + \frac{1}{7}[\text{CO}_2]} \times 100$$

Where [] is the number of moles produced or fed.

2.3. XRD measurement

The XRD pattern of the catalysts was observed at room temperature using X-ray diffraction equipment (Rigaku RINT 2100) with a Cu K α source.

2.4. BET surface area measurement

The BET surface areas of the catalysts, which were preheated at 473 K for 2 h, were measured using a static gas-adsorption apparatus equipped with a digital manometer.

2.5. UV–vis diffuse reflectance (DR) spectra

The UV–visible diffuse reflectance (DR) spectra of the Co supported catalysts were measured at room temperature using an electronic absorption spectrophotometer (Hitachi U-3210D) equipped with a 90 ϕ integral sphere (Hitachi 150-0902). The catalyst packed in the treatment portion of an in situ cell, connected to a vacuum line, was pretreated under various conditions before transferring for the DR measurement. The obtained DR data were transformed to the Kubelka–Munka function (F(R)) using an application program (Hitachi U-3210/U-3410).

2.6. Co K-edge X-ray absorption fine structure (XAFS)

The Co K-edge X-ray absorption fine structure (XAFS) spectra of the Co supported catalysts were obtained at the Spring-8 synchrotron radiation facility of the Japan Synchrotron Radiation Research Institute (JASRI). All the samples (ca. 0.2 g) were pressed into self-supported disks (diameter, ca 1 cm) without binder. The disks were degassed at 773 K for 30 min and treated at 773 K for 1 h in 150 Torr O₂ followed by degassing at room temperature for 30 min and enclosing under N₂ in a polyethylene pack. The Co K-edge absorption spectra were recorded in the transmission mode at room temperature under atmospheric pressure. The storage ring energy was 8.0 GeV and the ring current was 60–100 mA. A Si(3 1 1) double crystal monochromator was used.

3. Results and discussion

The main oxidation products of the gas-phase catalytic oxidation of benzyl alcohol over the Co catalysts supported on NaY and NaUSY zeolites were benzaldehyde and CO₂. Only a trace of benzene or toluene was detected under certain reaction conditions. No oxidation products were detected and benzyl alcohol was almost quantitatively recovered over only quartz sand as a diluent. The yield of the product was evaluated by averaging the values at the time on stream (TOS) of 2, 3, and 4 h. The carbon balance was usually more than 90%.

3.1. Dependence of the amount of Co impregnated on Co/NaUSY_{imp} and Co/NaY_{imp} catalysts

The dependences of the yields of benzaldehyde and CO₂ on the amount of impregnated Co were investigated at the reaction temperature of 623 K using both the Co/NaY_{imp} and the Co/NaUSY_{imp} catalysts (Fig. 1). The yield of benzaldehyde over the Co/NaUSY_{imp} catalyst increased with increasing the amount of impregnated Co although the degree in the increase largely declined at more than the Co amount of about 15 wt.%. The increase in the Co amount of the Co/NaY_{imp} catalyst also caused an increase in the yield of benzaldehyde until the Co amount of around 6 wt.%, but further increase in the amount of the impregnated Co caused a sharp decrease in the yield of benzaldehyde; the yield of benzaldehyde reached a maximum at the Co amount of ca. 6 wt.%. The NaUSY support was thus found to be more effective for the partial oxidation of benzyl alcohol than the NaY zeolite in the region of a higher amount of impregnated Co. The XRD pattern of the Co(20)/NaUSY_{imp} (Co, 20 wt.%) catalyst maintained a pattern based on Y-type one although the intensity became considerably low; also, the BET surface area declined from 631 m²/g of original NaUSY to 534 m²/g of the Co(20)/NaUSY_{imp}. The increase in the amount of Co also resulted in the detection of an XRD peak identified as Co oxides. Although the yield of CO₂ was low at the low amount of Co over both catalysts, the increase in the amount of impregnated Co brought about the gradual increase in the total oxidation products over the Co/NaUSY_{imp}.

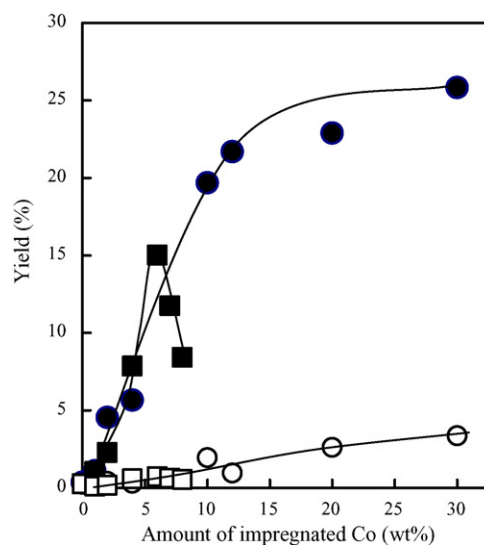


Fig. 1. Dependences of the yields of benzaldehyde and CO₂ on the amount of impregnated Co. Catalyst, 0.2 g; reaction temperature, 623 K; rounded symbol (●, ○), Cu/NaUSY_{imp}; square symbol (■, □), Cu/NaY_{imp}; full symbol (●, ■), yield of benzaldehyde; empty symbol (○, □), yield of CO₂.

Visual observation indicated that the increase in the amount of impregnated Co caused the color of the catalyst to become darker; thus from the pale of the Co(1)/NaUSY_{imp} to the dark grey of the Co(12)/NaUSY_{imp}. The UV–vis diffuse reflectance (DR) spectra of Co/NaUSY_{imp} catalysts were observed for samples with varying amounts of impregnated Co (Fig. 2). The DR spectrum of the Co(1)/NaUSY_{imp} (Fig. 2a, Fig. 2a' ≡ three times enlargement of spectrum a) indicates clearly triple peaks at 520, 580, and 675 nm. The DR peaks observed at around 510, and 550–650 nm of supported Co species were identified as Co²⁺

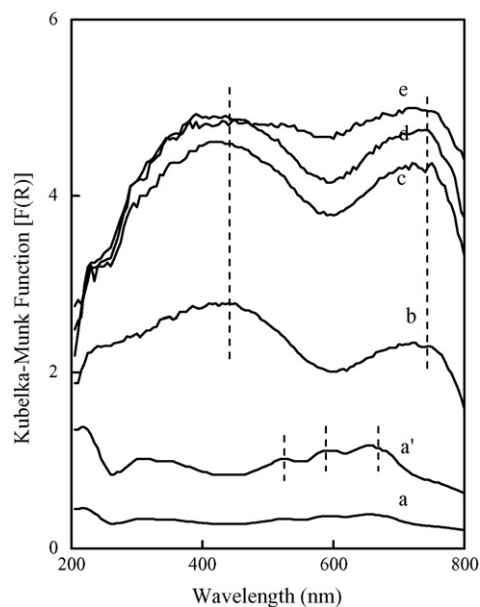


Fig. 2. DR spectra of Co/NaUSY_{imp} catalysts. All catalysts were treated at 773 K for 1 h in O₂ before measurement; (a) Co(1)/NaUSY_{imp}; (a'), spectrum a × 3; (b) Co(4)/NaUSY_{imp}; (c) Co(10)/NaUSY_{imp}; (d) Co(12)/NaUSY_{imp}; (e) Co(30)/NaUSY_{imp}.

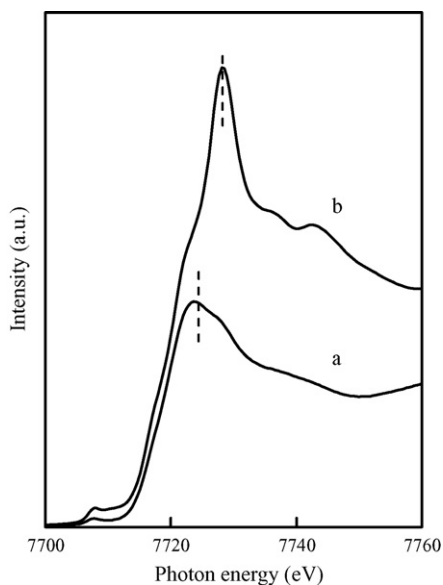


Fig. 3. X-ray absorption near edge spectra (XANES) of Co/NaUSY_{imp}. (a) Co(1)/NaUSY_{imp}; (b) Co(6)/NaUSY_{imp}.

ions coordinated with an octahedral and a tetrahedral configuration [17,18]. The increase in the amount of impregnated Co converted the DR spectrum to the broad peaks at 450 and 700–750 nm; the intensities of these broad peaks increased with increasing the Co amount and tended to level off for a great amount of Co. The DR broad peaks at 450 and 700–750 nm are assigned as Co₃O₄ [Co²⁺(Co³⁺)₂O₄] [17,18]. The Co species impregnated on the NaUSY were varied from Co²⁺ species to Co oxide containing high valence Co³⁺ species with increasing the amount of impregnated Co. The X-ray absorption near edge spectra (XANES) of both the Co(1)/ and Co(6)/NaUSY_{imp} catalysts are illustrated in Fig. 3. The absorption peak shifted from 7722 to 7728 eV accompanying the increase in the amount of the impregnated Cu. Jacobs et al. have reported [19] that the XANES of CoO and Co₃O₄ had an absorption peak at 7723 and 7728 eV, respectively. The results of the DR and the XANES of the Co/NaUSY_{imp} catalysts indicate that a portion of the Co²⁺ species impregnated on the NaUSY support are oxidized to form Co₃O₄ with the increase in the amount of impregnated Co. The formed Co₃O₄ species are suggested to be responsible to the catalytic activity of the partial oxidation of benzyl alcohol from the results of oxidation activity (Fig. 1).

3.2. Influence of potassium (K) added to the Co(6)/NaUSY_{imp} catalyst

The influence of an added alkali metal on the oxidation activity was investigated using the Co(6)/NaUSY_{imp} catalyst (Fig. 4). The yield of benzaldehyde increased with the increase in the added K/Co atomic ratio until the ratio of 4, but further increase in the added K/Co ratio caused a sharp decline in the yield of benzaldehyde. The XRD pattern based on the Y-type zeolite structure disappeared completely in the K(8)/Co(6)/NaY_{imp} (added K/Co = 8; Co, 6 wt.%) catalyst converting to a broad amorphous peak. The BET surface area of the K(8)/Co(6)–NaY_{imp} cat-

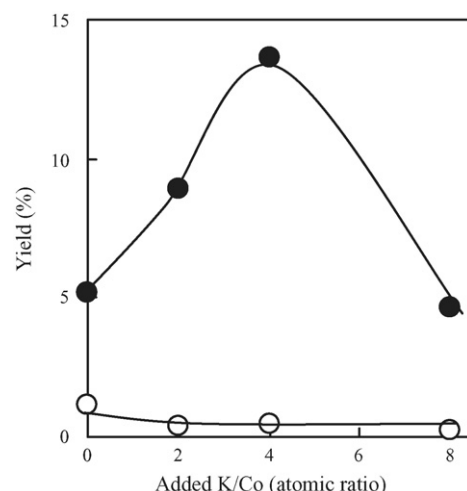


Fig. 4. Influence of K added to Co(6)/NaUSY_{imp} on the yields of benzaldehyde and CO₂. Catalyst, 0.2 g of K/Co(6)/NaUSY_{imp} (Co, 6 wt.%); reaction temperature, 623 K; (●) yield of benzaldehyde; (○) yield of CO₂.

alyst remarkably decreased to 35 m²/g from 595 m²/g of the Co(6)/NaUSY_{imp} without added K. The disruption of the Y-type zeolite structure of the K(8)/Co(6)/NaUSY_{imp} is thought to be strikingly promoted by the added K.

The XRD pattern of the Co(6)/NaUSY_{imp} without added K showed a peak at $2\theta = 37^\circ$ assigned as cobalt oxide, Co₃O₄, in addition to the XRD pattern based on a Y-type zeolite, in agreement with the DR spectra (Fig. 2). However, the increase in the amount of K added to the Co(6)/NaUSY_{imp} caused a gradual decrease in the XRD peak at $2\theta = 37^\circ$. Also, the XRD peak almost totally disappeared, together with the disappearance of the Y-type zeolite structure as aforementioned, in the XRD pattern of the K(8)/Co(6)/NaUSY_{imp}. The visual observations of the Co(6)/NaUSY_{imp} and the K(8)/Co(6)/NaUSY_{imp} were dark grey and blue violet, respectively. The DR spectra of the K(8)/Co(6)/NaUSY_{imp} showed triple peaks at 520, 580,

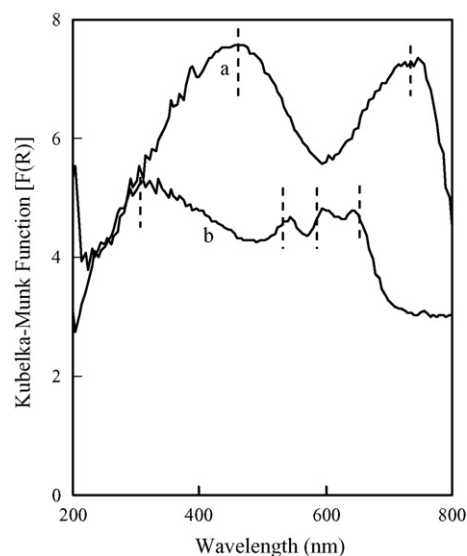


Fig. 5. DR spectra of Co(6)/NaUSY_{imp} and K(8)/Co(6)/USY_{imp}. (a) Co(6)/NaUSY_{imp}; (b) K(8)/Co(6)/USY_{imp}.

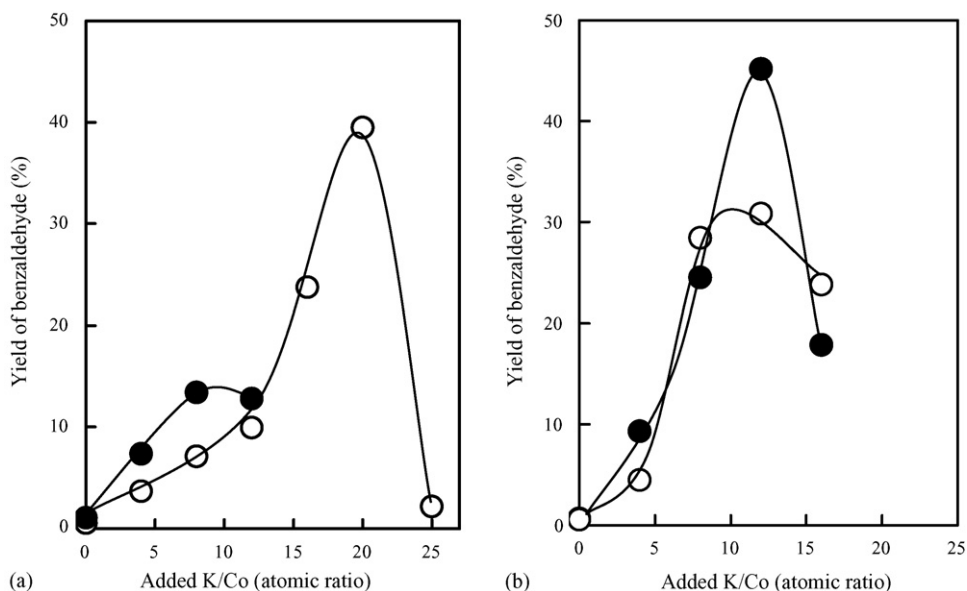


Fig. 6. Influence of added K/Co atomic ratio on the yield of benzaldehyde. Catalyst, 0.2 g; reaction temperature, 623 K. (a) (●) K/Co(1)/NaUSY_{imp}; (○) K/Co(1)-NaUSY_{ie}. (b) (●) K/Co(1)/NaY_{imp}; (○) K/Co(1)-NaY_{ie}.

and 675 nm and a broad peak at around 300 nm; similar DR peaks were observed using CoAl₂O₄ with a spinel structure, in contrast to the broad peaks at 450 and 750 nm based on Co₃O₄ in the Co(6)/NaUSY_{imp} catalyst (Fig. 5). These results of the DR spectra, together with the XRD results, suggest that the too much alkali metal (K) added to the Co(6)/NaUSY_{imp} catalyst has a function to reduce Co³⁺ (Co₃O₄) to Co²⁺ (CoAl₂O₄). The destruction of the Y-type structure and the reduction of Co species by adding a large amount of potassium (K) are thought to be the reason for the decline in the yield of benzaldehyde.

The curtailment of the amount of the added K is necessary to maintain the destruction of the Y-type zeolitic structure of the support to a minimum. The supported Co catalysts, in which the amount of impregnated or ion-exchanged Co was reduced to 1 wt.%, were used hereafter.

3.3. Influence of potassium (K) added to Co(1)/NaUSY_{imp}, Co(1)-NaUSY_{ie}, Co(1)NaY_{imp}, and Co(1)-NaY_{ie} catalysts

The influence of the added K/Co atomic ratio on the yield of benzaldehyde was investigated using the K/Co(1)/NaUSY_{imp} and the K/Co(1)-NaUSY_{ie} catalysts (Fig. 6a). The yields of CO₂ over these two catalysts were less than 0.6% and independent of the added K/Co atomic ratio (figure not depicted). Although the yield of benzaldehyde over the K/Co(1)/NaUSY_{imp} catalyst increased with increasing the added K/Co until a ratio of around 8, further increase in the K/Co ratio tended to decrease the yield. The XRD peaks, identified as the Y-type zeolite structure, were observed in the K(8)/Co(1)/NaUSY_{imp} catalyst. The maximum yield (13.4%) of benzaldehyde over the K(8)/Co(1)/NaUSY_{imp} (Added K/Co=8, Co, 1wt.%) catalyst was almost similar to that (13.6%; Fig. 4) over the K(4)/Co(6)-NaUSY_{imp} (Added K/Co=4, Co, 6wt.%). The K/Co(1)-NaUSY_{ie} catalyst had an appreciably higher catalytic activity for the partial oxidation than the corresponding one (K/Co(1)/NaUSY_{imp}) prepared

by impregnation. The maximum yield of benzaldehyde was obtained at the added K/Co ratio of around 20. The supporting method of cobalt on the NaUSY support was thus found to be a crucial factor for the partial oxidation although we can not reasonably interpret the account for the results. The other alkali metals added to the Co(1)-NaUSY_{ie} and the Co(1)/NaUSY_{imp} catalysts also promoted the catalytic activity of the partial oxidation of benzyl alcohol (Table 1). A good correlation was observed between the electronegativity of the added alkali metal and the yield of benzaldehyde. The added alkali metal/Co atomic ratio giving the maximum yield of benzaldehyde varies by the kind of added alkali metal [13].

The oxidation over 1 wt.% Co catalysts impregnated and ion-exchanged on NaY zeolites, instead of NaUSY, is illustrated in Fig. 6b. The yields of CO₂ over the two catalysts did

Table 1
Influence of an alkali metal added to Co(1)-NaUSY_{ie} and Co(1)/NaUSY_{imp} catalysts^a

Catalysts	Yield of benzaldehyde (%)	Yield of CO ₂ (%)
Co(1)-NaUSY _{ie}	0.55	0.19
Li(4)/Co(1)-NaUSY _{ie}	1.3	0.19
Na(4)/Co(1)-NaUSY _{ie}	2.5	0.23
K(4)/Co(1)-NaUSY _{ie}	3.8	0.46
Rb(4)/Co(1)-NaUSY _{ie}	10.7	0.18
Cs(4)/Co(1)-NaUSY _{ie}	11.6	0.59
Co(1)/NaUSY _{imp}	1.1	0.22
Li(8)/Co(1)/NaUSY _{imp}	2.2	0.50
Na(8)/Co(1)/NaUSY _{imp}	5.3	0.83
K(8)/Co(1)/NaUSY _{imp}	13.4	0.12
Rb(8)/Co(1)/NaUSY _{imp}	10.6	0.57
Cs(8)/Co(1)/NaUSY _{imp}	10.1	0.19

^a Reaction conditions: catalyst, 0.2 g; Co, 1 wt.%; added alkali metal/Co atomic ratio, 4 for Co(1)-NaUSY_{ie}, 8 for Co(1)/NaUSY_{imp}; reaction temperature, 623 K.

Table 2
Influence of an alkali metal added to Co(1)-NaY_{ie}

Catalysts	Yield of benzaldehyde (%)	Yield of CO ₂ (%)
Co(1)-NaY _{ie}	0.55	0.19
Li(4)/Co(1)-NaY _{ie}	2.2	Trace
Na(4)/Co(1)-NaY _{ie}	3.5	Trace
K(4)/Co(1)-NaY _{ie}	4.5	0.59
Rb(4)/Co(1)-NaY _{ie}	7.3	0.32
Cs(4)/Co(1)-NaY _{ie}	11.3	0.59

Reaction conditions: catalyst, 0.2 g; Co, 1 wt.%; added alkali metal/Co atomic ratio, 4; reaction temperature, 623 K.

not exceed 0.9% irrespective of the added K/Co atomic ratio (figure not shown). The yields of benzaldehyde over both the K/Co(1)/NaY_{imp} and K/Co(1)-NaY_{ie} catalysts increased with the increase in the K/Co atomic ratio and passed through a maximum at a ratio of around 12. The K/Co(1)/NaY_{imp} catalyst had a higher activity for the partial oxidation than the counterpart prepared by an ion-exchange method. The XRD peaks, based on the Y-type zeolite structure, were clearly observed in both the K(12)/Co(1)/NaY_{imp} and K(12)/Co(1)-NaY_{ie} catalysts, but the intensity of the XRD peaks of the latter catalyst at the K/Co ratio of 16 were considerably low. The BET surface areas of the K/Co(1)-NaY_{ie} and the K/Co(1)/NaY_{imp} catalysts gradually decreased with the increase of the added K/Co atomic ratio.

The potassium (K) added to the 1 wt.% Co impregnated and ion-exchanged NaUSY and NaY catalysts was confirmed to selectively promote the partial oxidation of benzyl alcohol to benzaldehyde. A considerably higher yield of benzaldehyde was obtained over the Co catalyst supported with a low amount of Co and added K than the Co catalyst supported with a high amount of Co (Fig. 1 vs. Fig. 6a and b). However, the supporting method and the selection of a Y-type support with different Si/Al ratios had a large effect on the catalytic activity for the partial oxidation. The best performed catalyst among the catalytic systems investigated in this study was the K(12)/Co(1)/NaY_{imp}: yield of benzaldehyde, 45.2%; selectivity of benzaldehyde, 99.0% (cf. Co(1)/NaY_{imp} catalyst without added K: yield of benzaldehyde, 0.65 %; the selectivity of benzaldehyde, 61.7%).

Table 2 shows the influence of an alkali metal added to the Co(1)-NaY_{ie} catalyst at the added alkali metal/Co = 4 on benzyl alcohol oxidation. As in Table 1, the yield of benzaldehyde increased with the decrease in the electronegativity, thus the increase in the electron donation, of the added alkali metal. The added alkali metal was confirmed to promote the partial oxidation although the added alkali metal/Co ratio giving a maximum yield seems to differ by choice of the added alkali metal.

3.4. Effect of interaction of active Co species and added potassium (K) on the oxidation of benzyl alcohol

An alkali metal such as potassium (K) was found to selectively promote the partial oxidation activity of the supported Co catalysts with a low amount of Co. To investigate whether the added alkali metal functions independently or acts in concert with the Co species, the catalytic activity of the physically mixed catalyst of K/NaY_{imp} and Co(1)/NaY_{imp} was compared

Table 3
Catalytic activity of physically mixed catalyst of Co(1)/NaY_{imp} and K/NaY_{imp}^a

Catalysts	Yield of benzaldehyde (%)	BET surface area (m ² /g)
Co(1)/NaY _{imp}	0.65	520
K/NaY _{imp} ^b	0.50	342
Co(1)/NaY _{imp} + K/NaY _{imp} ^b	0.83	431 ^c
K(8)/Co(1)/NaY _{imp}	24.5	484

^a Reaction conditions: catalyst, 0.2 g; Co, 1 wt.%; added K/Co atomic ratio, 8; reaction temperature, 623 K.

^b Impregnated K, same as the K amount added to the K(8)/Co(1)/NaY_{imp} catalyst.

^c Arithmetic average of the BET surface areas of Co(1)/NaY_{imp} and K/NaY_{imp}.

to that of the K/Co(1)/NaY_{imp} catalyst, together with the BET surface areas of these catalysts (Table 3). The yield of CO₂ was less than 0.8% irrespective of the catalysts used here. The Co(1)/NaY_{imp} or the K/NaY_{imp} itself separately had little catalytic activity for the oxidation of benzyl alcohol. The physically mixed catalyst of the Co(1)/NaY_{imp} and the K/NaY_{imp} [Co(1)/NaY_{imp} + K/NaY_{imp}] also had only a low catalytic activity, in contrast to the catalytic activity of the K(8)/Co(1)/NaY_{imp} catalyst (yields of benzaldehyde and CO₂, 24.5% and 0.79%, respectively). The results obtained in Table 3 clearly indicate that only K added microscopically in contact with the Co species is able to promote the partial oxidation of benzyl alcohol; in other words, the direct interaction of the added K to the Co species causes the selective promotion of the catalytic activity for the partial oxidation.

The effect of the catalytic activity for the partial oxidation on the order in the impregnation of Co and K was investigated using three catalysts (Table 4): the Co impregnated NaY catalyst followed by impregnating K [K(8)/Co(1)/NaY_{imp}], the K impregnated NaY catalyst followed by impregnating Co [Co(1)/K(8)/NaY_{imp}], and a co-impregnation catalyst of Co and K [K(8)-Co(1)/NaY_{imp}]. The BET surface area of the K/Co(1)/NaY_{imp} catalyst was higher than those of the other two catalysts. All the XRD patterns of the three catalysts were almost similar to that of NaY zeolite. The order in the impregnation of Co and K was found not to basically affect the partial oxidation activity although the yield of benzaldehyde over the co-impregnated catalyst was somewhat lower than the sequentially impregnated counterparts.

Table 4
Catalytic activity of the Co catalysts impregnated in different order of Co and K^a

Catalysts	Yield of benzaldehyde (%)	BET surface area (m ² /g)
K(8)/Co(1)/NaY _{imp} ^b	24.5	484
Co(1)/K(8)/NaY _{imp} ^c	24.0	351
K(8)-Co(1)/NaY _{imp} ^d	16.8	343

^a Reaction conditions: catalyst, 0.2 g; Co, 1 wt.%; added K/Co atomic ratio, 8; reaction temperature, 623 K.

^b Impregnation of Co followed by impregnating K.

^c Impregnation of K followed by impregnating Co.

^d Co-impregnation of K and Co.

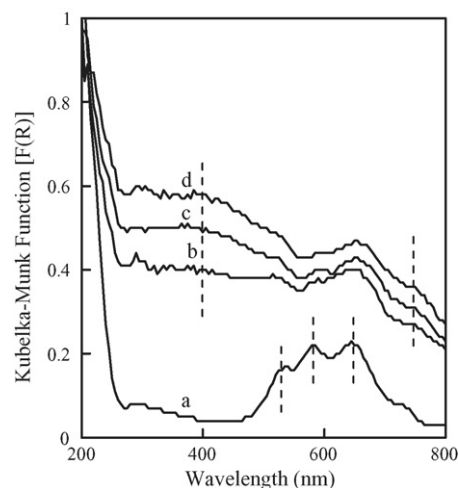


Fig. 7. DR spectra of alkali metal added Co(1)-NaY_{ie} catalysts. Amount of supported Co, 1 wt.%; added alkali metal/Co atomic ratio, 4; (a) Co(1)-NaY_{ie}; (b) Na(4)/Co(1)-NaY_{ie}; (c) K(4)/Co(1)-NaY_{ie}; (d) Cs(4)/Co(1)-NaY_{ie}.

3.5. Influence of an added alkali metal on supported Co species

The DR spectra of the alkali metal added Co(1)-NaY_{ie} catalysts with a low amount of Co were observed at the added alkali metal/Co atomic ratio of 4, together with the corresponding Co(1)-NaY_{ie} without an added alkali metal (Fig. 7). The DR spectrum of the Co(1)-NaY_{ie} catalyst (Fig. 7a) clearly showed three peaks at around 600 nm identified as Co²⁺ species as mentioned previously (3.2). The DR spectrum was changed by adding an alkali metal to the Co(1)-NaY_{ie} catalyst (Fig. 7b–d). Two broad DR bands at around 400 and 750 nm, which are attributed to a cobalt oxide, Co₃O₄ [Co²⁺(Co³⁺)₂O₄], were appeared by adding an alkali metal, in addition to the triplet peaks at around 600 nm, irrespective of the kind of the added alkali metal. The addition of the alkali metal to the Co(1)-NaY_{ie} brought about an increase in the yield of benzaldehyde as described in Table 2. The formed Co₃O₄ [Co²⁺(Co³⁺)₂O₄] is thus thought to be responsible for the catalytic activity for the benzaldehyde formation.

The variation in the DR spectra of the K added Co(1)-NaY_{ie} catalyst [K/Co(1)-NaY_{ie}] with a low amount of Co was observed by varying the added K/Co atomic ratio (Fig. 8). The increase in the ratio caused an increase in the broad peaks at around 400 and 750 nm, although the degree of the increase in the broad bands tended to decrease with the increase in the added K/Co ratio as illustrated in Fig. 8. The increase in the broad bands attributed to Co₃O₄ [Co²⁺(Co³⁺)₂O₄] with the increase in the added K/Co atomic ratio qualitatively correlates to the increase in the yield of benzaldehyde with increasing the added K/Co atomic ratio up to a ratio of around 12, as illustrated in Fig. 6b.

The addition of an alkali metal to the supported Co catalyst was found to promote the formation of the cobalt oxide, Co₃O₄ [≡Co²⁺(Co³⁺)₂O₄], even in the presence of a low amount of supported Co. The added alkali metal is thus suggested to transfer an electron to the neighbor Co species to form an electron rich Co species which has high oxygen affinity and easily forms the

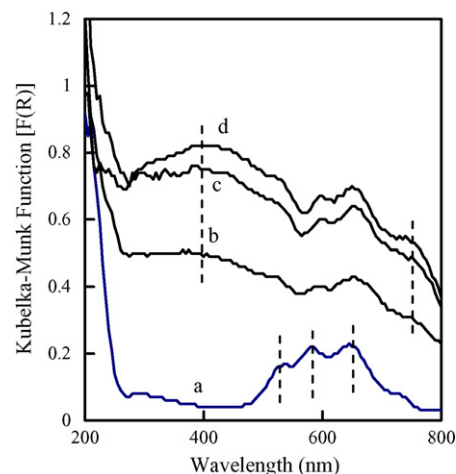


Fig. 8. Variation in DR spectra of K/Co(1)-NaY_{ie} by the added K/Co atomic ratio. Amount of supported Co, 1 wt.%; (a) added K/Co=0 (Co(1)-NaY_{ie}); (b) added K/Co=4 (K(4)/Co(1)-NaY_{ie}); (c) added K/Co=8 (K(8)/Co(1)-NaY_{ie}); (d) added K/Co=12 (K(12)/Co(1)-NaY_{ie}).

corresponding cobalt oxide as shown from the variation in the DR spectra of Co(1)-NaY_{ie} catalysts with and without the added K. The reaction results obtained in the present study indicates that the formed Co₃O₄ [≡Co²⁺(Co³⁺)₂O₄] is responsible for the catalytic activity for the partial oxidation of benzyl alcohol.

4. Conclusions

The yield of benzaldehyde over the Co catalysts (Co/NaUSY_{imp}) impregnated on NaUSY zeolite increased with the increase in the amount of impregnated Co, but the counterpart catalyst using NaY zeolite support (Co/NaY_{imp}) deeply deactivated at the high amount of impregnated Co. The increase in the amount of Co impregnated on the NaUSY support changed the supported Co species from tetrahedral Co²⁺ species to Co₃O₄ [Co²⁺(Co³⁺)₂O₄]. The formed Co oxide increased with increasing the amount of the impregnated Co. The addition of potassium (K) to the Co(6)/NaUSY_{imp} (Co, 6 wt.%) catalyst promoted the yield of benzaldehyde, but high amount of added K destroyed the zeolitic structure of the NaUSY support and deactivated the partial oxidation. The addition of an alkali metal to the Co catalysts ion-exchanged or impregnated on NaY and NaUSY supports (Co-NaY_{ie}, Co/NaY_{imp}, Co-NaUSY_{ie}) with a low amount of Co (1 wt.%) promoted the partial oxidation of benzyl alcohol, although the oxidation activity of the K/Co(1)/NaUSY_{imp} catalyst declined at the higher added alkali metal/Co atomic ratios as that of the K/Co(6)/NaYSY_{imp}. However, the activity of the K/Co(1)/NaUSY_{imp} catalyst increased up to a ratio of around 12, in contrast to the K/Co(6)/NaYSY_{imp} catalyst whose activity decreased at a ratio larger than 4. The added alkali metal microscopically neighbored next to the Co species was responsible for selectively promoting the yield of benzaldehyde. The role of the added alkali was supposed to promote the formation of Co₃O₄ [Co²⁺(Co³⁺)₂O₄], the Co species which directly participates in the partial oxidation, even in the presence of the low amount of Co.

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