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Oxidation activity of cerium supported NaZSM-5 zeolites with and without added alkali metals in the gas-phase catalytic oxidation of benzyl alcohol

Arihiro Kanada,[a] Nao Idaka,[a] Satoru Nishiyama,[a] Shigeru Tsuruya*[a] and Mitsuo Masai[b]

[a] *Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Nada, Kobe 657, Japan. E-mail: tsuruya@cx.kobe-u.ac.jp*
[b] *Department of Applied Physics and Chemistry, The Fukui University of Technology, Gakuen, 3-6-1, Fukui, 910, Japan*

Received 9th September 1998, Accepted 16th November 1998

The gas-phase catalytic oxidation of benzyl alcohol was carried out over low [Ce_L, $\sim 1 \times 10^{-2}$ mmol (g-NaZSM-5)$^{-1}$] and high [Ce_H, $\sim$1–2 mmol (g-NaZSM-5)$^{-1}$] Ce supported NaZSM-5 zeolites and alkali metal added counterparts. The Ce was supported on NaZSM-5 zeolites by both ion-exchange (Ce_L-NaZSM-5) and impregnation (Ce_L- and Ce_H/NaZSM-5) methods. The alkali metal added to the low and high Ce supported NaZSM-5 catalysts was found to be quite different in influence on the catalytic activity of benzyl alcohol oxidation. The addition of alkali metal to the Ce_L- and/or Ce_L/NaZSM-5 zeolites was found to promote selectively catalytic activity for the partial oxidation of benzyl alcohol. The addition of the alkali metal caused an increase in the amount of O_2 uptake of the prereduced Ce_L- and/or Ce_L/NaZSM-5 catalysts. A correlation was observed between the amount of O_2 uptake and the amount of alkali metal added to the Ce_L- and/or Ce_L/NaZSM-5 catalysts. The alkali metal added to the Ce_L- and/or Ce_L/NaZSM-5 catalysts was suggested to promote the mobility of the oxygen species in the low Ce supported catalysts, whose oxygen species are considered to play an important role in benzaldehyde formation. The alkali metal added to the Ce_H/NaZSM-5 catalysts inversely tended to decrease the oxidation activity. The addition of the alkali metal to the Ce_H/NaZSM-5 catalyst made the particle size of CeO_2 formed in the Ce_H/NaZSM-5 larger, and the redox ability of the oxidic cerium lower through the inhibition of the uptake of O_2.

Cerium, one of the lanthanide rare metals, has been applied[1] as one of the ternary components of a catalyst for the control of automobile exhaust. It is well known that cerium species have functions of reversible storage and release of gaseous oxygen because the cerium ion has a low redox potential (1.61 eV [2]) between Ce^{3+} and Ce^{4+}. The $Ce_{0.8}Zr_{0.2}O_2$ catalyst has been recently reported[3] to have a greater capacity for oxygen storage than pure CeO_2. Some interesting synthetic reactions in which cerium species are utilized as active catalytic components have been reported. Acylation of phenol has been reported[4] using Ce supported ZSM-5 catalysts, in addition to the corresponding Co, and Cu supported ZSM-5 zeolites. Cerium oxide has been found[5] to be catalytically active for the methylation of phenol. Cerium oxide including a small amount of CuO has been reported[6] to have higher catalytic activity for CO oxidation and higher heat resistance than its pure CeO counterpart, because the former system easily forms the larger CeO crystallite. NO decomposition has been reported[7] to be enhanced using a Cu supported NaZSM-5 catalyst with added Ce. Lanthanide rare metal ion-exchanged Y type zeolites,[8] Ce-ZSM-5 zeolites,[8] and Ce-ZSM-5 zeolites with alkaline-earth metals[9] have also been studied as catalysts for NO decomposition.

We have studied the oxidation activity of Cu supported Y type[10] and ZSM-5 zeolite[11,12] catalysts using the gas-phase catalytic oxidation of benzyl alcohol as a test reaction. The addition of alkali metal to the Cu supported zeolites[13–16] and SiO_2 [17] has been reported to greatly enhance the catalytic activity of benzyl alcohol oxidation, particularly the partial oxidation activity. The alkali metals added to the Cu supported zeolites have been reported[14–15] to play an important role in the increase in the amount of O_2 uptake of the prereduced catalysts, whose sorbed oxygen species were suggested to be responsible for the partial oxidation of benzyl alcohol.

The purpose of this paper is to study the oxidation activities of cerium supported NaZSM-5 zeolites and the alkali metal added counterparts in the oxidation of benzyl alcohol, and to clarify the role in the oxidation played by the added alkali metals. The oxidation activities obtained by the gas-phase catalytic oxidation of benzyl alcohol are discussed in connection with the oxygen storage abilities of the catalysts estimated by the O_2 uptake measurements. The diffuse reflectance (DR) spectra of the Ce supported NaZSM-5 catalysts were measured to investigate the redox behavior of the Ce species on the NaZSM-5 zeolites.

Experimental

Catalysts

NaZSM-5 zeolite was synthesized according to a patent.[18] To prepare 100% Na ion-exchange ZSM-5, the obtained NaZSM-5 zeolite was treated two times at 342-358 K for 1 h with an aqueous solution of 1 mol l^{-1} $NaNO_3$. The filtered NaZSM-5 zeolite was washed with deionized water, dried at room temperature overnight, and calcined at 773 K for 5 h. Ce ion-exchanged NaZSM-5 (Ce-NaZSM-5) zeolite was prepared by ion-exchanging (1–4 times) at 353–362 K for 2–5 h with an aqueous solution of $Ce(CH_3COO)_3 \cdot H_2O$ (Nakalai tesque, guaranteed reagent). The prepared Ce-NaZSM-5 zeolite was filtered, washed with deionized water, dried overnight at 393 K, and calcined at 773 K for 5 h in air flow. Ce impregnated NaZSM-5 (Ce/NaZSM-5) zeolites were prepared by immersing the NaZSM-5 zeolite in an aqueous solution of $Ce(CH_3COO)_3 \cdot H_2O$ (Nakalai tesque, guaranteed reagent) and evaporating the solvent water, followed by calcination at 773 K for 5 h. The Si : Al atomic ratio of the prepared NaZSM-5 zeolite was determined by dissolving the sample homogeneously with one or two drops of neat hydrogen fluoride (Hashimoto Chemical, 47% content, guaranteed reagent) and by using an atomic absorption (AA) spectrophotometer (Shimazu Model AA-630-01). The amount of ion-exchanged Ce was determined by subtracting the amount of Na content in Ce-NaZSM-5 from that of the NaZSM-5 zeolite, of which Na amounts were analyzed using the AA method. Alkali metal added Ce-NaZSM-5 zeolite was prepared by immersing the Ce-NaZSM-5 in an aqueous solution of alkali acetate (Nakarai tesque, guaranteed reagent), evaporating the solvent water, drying overnight at 393 K, and calcining at 773 K for 3 h in air flow.

XRD measurement of catalysts

Powder XRD measurements of the synthesized NaZSM-5 zeolite and various Ce supported NaZSM-5 zeolites were conducted at room temperature by a Rigaku XRD equipment using Cu-Kα as the X-ray source.

Gas-phase catalytic oxidation of benzyl alcohol

The oxidation reaction of benzyl alcohol (Nakalai tesque, guaranteed reagent) was performed using a conventional continuous fixed-bed Pyrex glass reactor (id 15 mm). Before the oxidation, the catalyst was calcined at 773 K for 2 h in an air flow. The reaction was started by supplying benzyl alcohol to a micro feeder. Typical reaction conditions are as follows: $W/F = 21.7$ g-cat min mol^{-1} (W, catalyst weight; F, total mole flow rate), $W = 0.5$ g, $F = 0.023$ mol min^{-1}, $N_2 : O_2$: benzyl alcohol = 32 : 3 : 1 (mole ratio). The liquid products and unreacted benzyl alcohol were collected by trapping at 223 K with a refrigerant (liquid N_2 + diethyl malonate) and analyzed[15] by a Shimazu Model GC-8A gas chromatograph after adding 1 cm^3 of dimethylformamide (Nakalai tesque, guaranteed reagent) as an internal standard. The gaseous products were introduced into a gas sampler (1 cm^3) through a 6-way bulb and analyzed by an intermediate-cell method[15] using a gas chromatograph (Shimazu Model GC-8A). The definitions of the conversion of benzyl alcohol, the yields and selectivities of the products, and the carbon balance have been described elsewhere.[15] The carbon balances in this study were 80–100%, usually greater than 90%.

Measurement of O_2 uptake

The amount of O_2 uptake of the prereduced catalysts was measured using a constant-volume type semi-micro gas sorption apparatus with a capillary sample tube. After the catalyst (0.05 g) was degassed (less than 0.1 Pa) at 773 K for 0.5 h, the catalyst was treated at 773 K for 1 h under an O_2 atmosphere (20 kPa) followed by degassing at 773 K for 1 h. The catalyst was then treated at 773 K for 1 h under CO atmosphere (20 kPa) followed by degassing at 773 K for 1 h. The dead volume of the apparatus was measured by introducing He gas (1.3 kPa) followed by degassing at the measurement temperature for 0.5 h. The total amount of O_2 uptake was measured after the introduction of O_2 (2.6 kPa) at the measurement temperature and the attainment of equilibrium. The amount of reversible O_2 uptake was measured by repeating this operation after degassing at the measurement temperature for 1 h. The amount of irreversible O_2 uptake was defined as the difference between the total and the reversible amounts of O_2 uptake.

Measurement of diffuse reflectance (DR) spectra

The DR spectra of Ce supported NaZSM-5 zeolites were observed using an electronic absorption spectrophotometer (Hitachi Model U-3210D) attached to an integral sphere (60 ϕ, Hitachi Model 150-0902). The sample was placed in an *in situ* quartz cell, connected to a vacuum line with a side arm in which the sample can be treated at various temperatures and atmospheres. The obtained reflectances were converted to Kubelka–Munk (KM) functions using an applied program.

Temperature programmed oxidation (TPO) of ethanol

The TPO of ethanol was conducted using thermogravimetry (TG)-differential thermal analysis (DTA) equipment (Shimazu Model DTG-40). The catalyst (10 mg) was calcined at 773 K for 1 h in an air flow (30 cm^3 min^{-1}), followed by cooling at room temperature. The TPO was started by supplying ethanol (Nakalai tesque, guaranteed reagent) in a microfeeder under an air flow (30 cm^3 min^{-1}) with a programmed temperature of 20 K min^{-1}.

Results

Gas-phase catalytic oxidation of benzyl alcohol over low Ce supported NaZSM-5

No products were observed and the starting material was quantitatively recovered when the oxidation of benzyl alcohol was performed at 673 K using only quartz sand (diluent for a catalyst). The main oxidation products were a partial oxidation product, benzaldehyde and a perfect oxidation product, CO_2. No CO was observed in the gaseous product.[14] Traces of benzene and/or toluene were detected under some reaction conditions. The yield of a product obtained in this paper is the average value during the process time of 2–4 h.

The influence of the amount of the Ce supported on NaZSM-5 zeolites by the ion-exchange (Ce_L-NaZSM-5) and the impregnation (Ce_L/NaZSM-5) methods on the product yields is illustrated in Fig. 1. A subscript L is added to Ce ($\sim 10^{-2}$ mmol (g-NaZSM-5)$^{-1}$) to distinguish from high Ce (~ 1 mmol (g-NaZSM-5)$^{-1}$) impregnated NaZSM-5 zeolite (Ce_H/NaXZSM-5) described later. The yields of both benzaldehyde and CO_2 increased with an increase in the amount of supported Ce, irrespective of the supporting method of Ce.

The effect of alkali metal(4) (added alkali metal : Ce atomic ratio, 4) added Ce_L(22)-NaZSM-5 {ion-exchange of Ce, 22%

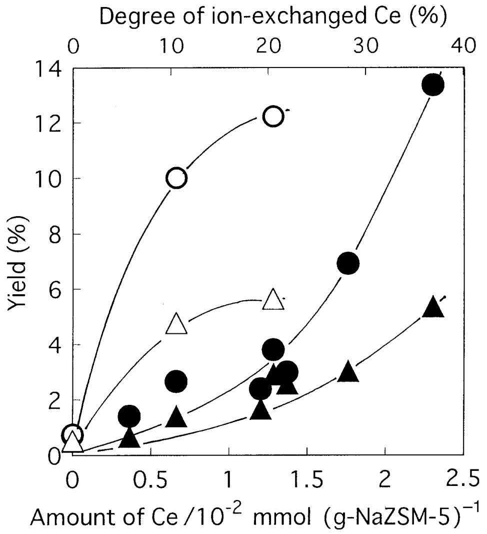

Fig. 1 Dependence of oxidation activities of Ce supported NaZSM-5 catalysts on the amount of supported Ce. Catalyst, 0.5 g; reaction temperature, 673 K; ○, △, Ce_L/NaZSM-5; ●, ▲, Ce_L-NaZSM-5; ○, ●, yield of benzaldehyde; △, ▲, yield of CO_2.

[1.28 × 10^{-2} mmol (g-NaZSM-5)$^{-1}$]} zeolite on both the yield and selectivity of benzaldehyde at the reaction temperature of 673 K is shown in Table 1. The addition of alkali metal, irrespective of the kind of alkali metal, caused an increase in both the yield and selectivity of benzaldehyde. Although the yield of CO_2 also increased by adding alkali metal to the Ce_L-NaZSM-5 catalyst, the extent of the increase in the CO_2 yield was lower than that of the benzaldehyde yield. The yield of benzaldehyde did not increase so much by adding Rb (the same amount of Rb as the Rb(4) added Ce_L(22)-NaZSM-5) to NaZSM-5 support without the Ce species.

The oxidation activity of the physically mixed catalytic system of Ce_L-NaZSM-5 (0.25 g) and Rb impregnated NaZSM-5 (Rb/NaZSM-5, 0.25 g) zeolites was compared with that of the Rb(4) added Ce_L(22)-NaZSM-5 (0.5 g) catalyst (Table 2). The amounts of Ce and Rb components were almost the same in both catalytic systems. A higher oxidation activity was obtained by the spatially closer contact between Ce and Rb.

The dependence of the added alkali metal : Ce atomic ratio (amount of Ce, constant) on the catalytic activity was investigated using K and Rb as the additives to the Ce ion-exchanged NaZSM-5 (Ce_L-NaZSM-5) catalyst (Fig. 2). The yield of benzaldehyde was found to increase with an increase in the added K (or Rb) : Ce atomic ratio and passed through a maximum value at the atomic ratio of around 4. The addition of K or Rb to the Ce_L-NaZSM-5 catalyst also caused an increase in the yield of CO_2, but to a considerably lesser extent than that of benzaldehyde. Thus, the selectivity for the partial oxidation was confirmed to increase by adding alkali metal to the Ce_L-NaZSM-5 zeolite. Fig. 3 illustrates the dependence of the yields of both products on the Rb : Ce atomic ratio using a Ce and Rb co-impregnated NaZSM-5 [(Rb–Ce_L)/NaZSM-5] catalyst (the Ce and Rb amounts were the same as those of Rb(4) added Ce_L(22)-NaZSM-5). The oxidation activity of (Rb–Ce_L)/Na-ZSM-5 catalyst was substantially similar to that of the Rb added Ce_L-NaZSM-5 catalyst in which the Ce and Rb were supported by ion-exchange and impregnation methods, respectively. The effect of the supporting method and/or the supporting order of Ce and/or Rb species on both yields at the reaction temperatures of 573, 623 and 673 K is summarized in Table 3: where Ce_L/Rb/NaZSM-5 (Rb and Ce were impregnated in this order), Rb/Ce_L/NaZSM-5 (Ce and Rb were impregnated in this order), Rb/Ce_L-NaZSM-5 (Ce was at first ion-exchanged, then Rb was impregnated), and (Rb–Ce_L)/NaZSM-5 (Ce and Rb were co-impregnated) zeolites were attempted as catalysts. The amounts of Ce and Rb supported on NaZSM-5 were the same in all the catalysts (Ce, 1.28 × 10^{-2} mmol (g-NaZSM-5); Rb : Ce atomic ratio, 4). All the catalysts studied here gave a higher yield of benzaldehyde than the Ce_L-NaZSM-5 (only Ce was ion-exchanged) or Ce_L/NaZSM-5 (only Ce was impregnated) catalyst. The degree of the increase in the yield of benzaldehyde at higher reaction temperatures over alkali metal added Ce supported NaZSM-5 catalysts, regardless of the supporting method, was higher than that over the corresponding catalysts without the added alkali metal. The addition of alkali metal to the Ce supported NaZSM-5 catalysts tended to prohibit the formation of CO_2 even at higher reaction temperatures. The alkali metal addition thus was found to give both the high benzaldehyde yield and the high selectivity for benzaldehyde at higher reaction temperature. The benzaldehyde yield at 673 K of the catalyst (Ce_L/Rb/NaZSM-5) where Rb and Ce were supported by impregnation in this order was distinctly higher than that of the other catalysts

Table 1 Effect of alkali metal added to Ce_L-NaZSM-5 catalyst on the yield and selectivity of benzaldehyde[a]

	Benzaldehyde	
Catalyst	Yield (%)	Selectivity (%)
Ce_L-NaZSM-5	3.6	47.8
Li(4) added Ce_L-NaZSM-5	4.9	63.7
Na(4) added Ce_L-NaZSM-5	6.2	58.0
K(4) added Ce_L-NaZSM-5	16.2	68.2
Rb(4) added Ce_L-NaZSM-5	25.1	78.5
Cs(4) added Ce_L-NaZSM-5	13.5	77.2
NaZSM-5	0.8	53.0
Rb/NaZSM-5[b]	2.6	74.0

[a] Catalyst, 0.5 g of alkali metal(4) added Ce_L(22)-NaZSM-5 (Ce, 1.28 × 10^{-2} mmol (g-NaZSM-5)$^{-1}$; alkali metal : Ce atomic ratio = 4); reaction temperature, 673 K. [b] The added Rb is the same amount as the alkali metal added Ce_L-NaZSM-5 zeolites.

Table 2 Oxidation activity of physically mixed catalytic system[a]

Catalyst[b]	Benzaldehyde Yield (%)	CO_2 Yield (%)
Ce_L(22)-NaZSM-5 (0.25 g) + Rb-NaZSM-5 (0.25g)	16.1	2.0
Rb(4) added Ce_L(22)-NaZSM-5 (0.5 g)	25.1	6.5

[a] Reaction temperature, 673 K; the amounts of Ce and added RB are almost the same in both catalytic systems.

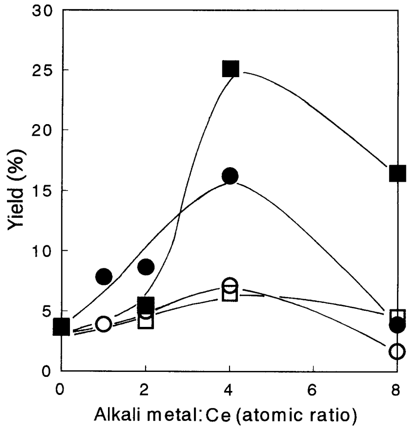

Fig. 2 Dependence of the added alkali metal : Ce atomic ratio on the oxidation activity of alkali metal added Ce_L-NaZSM-5 catalyst. Catalyst, 0.5 g; ●, ○, K added Ce_L-NaZSM-5(Ce, 1.28 × 10^{-2} mmol (g-NaZSM-5)$^{-1}$); ■, □, Rb added Ce_L-NaZSM-5 (Ce, 1.28 × 10^{-2} mmol (g-NaZSM-5)$^{-1}$); reaction temperature, 673 K; ●, ■, yield of benzaldehyde; ○, □, yield of CO_2.

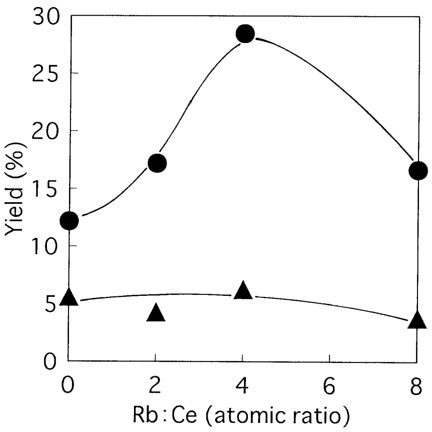

Fig. 3 Dependence of the added Rb : Ce atomic ratio on the oxidation activities of (Rb–Ce_L)/NaZSM-5 catalyst. Catalyst, 0.5 g of (Rb–Ce_L)/NaZSM-5 (Rb, Ce (1.28 × 10^{-2} mmol (g-NaZSM-5)$^{-1}$) co-impregnated NaZSM-5); reaction temperature, 673 K; ●, yield of benzaldehyde; ▲, yield of CO_2.

Table 3 Dependence of reaction temperature on the yield of benzaldehyde[a]

Catalyst[b]	Reaction temperature/K	Benzaldehyde Yield (%)	Benzaldehyde Selectivity (%)	CO_2 Yield (%)
Ce_L-NaZSM-5	573	0.3	46.9	0.3
	623	0.7	52.5	0.6
	673	3.6	47.8	3.7
Ce_L/NaZSM-5	573	0.6	72.8	0.2
	623	4.9	87.3	0.7
	673	12.2	66.6	5.6
Rb/Ce_L-NaZSM-5	573	0.3	78.7	0.1
	623	1.7	82.7	0.3
	673	25.1	78.5	6.5
Rb/Ce_L/NaZSM-5	573	1.3	80.7	0.3
	623	4.9	87.4	0.7
	673	25.5	81.0	6.5
(Rb-Ce_L)/NaZSM-5	573	1.1	90.8	0.1
	623	5.1	91.7	0.4
	673	28.5	81.9	6.3
Ce_L/Rb/NaZSM-5	573	2.0	83.8	0.4
	623	4.9	93.6	0.3
	673	36.8	84.5	6.7

[a] Catalyst, 0.5 g. [b] Amount of Ce, 1.28×10^{-2} mmol (g-NaZSM-5)$^{-1}$; Rb : Ce atomic ratio, 4.

(Fig. 4). This result might indicate that the catalyst in which the active Ce species are not shielded by a secondary component and exposed in the outer surface is a favored one. The yields of CO_2 did not vary significantly among the catalysts and were less than 10% (Fig. 4).

O_2 uptake of prereduced Ce supported NaZSM-5 zeolites

Fig. 5(a) and (b) illustrate the amount of O_2 uptake of the prereduced Ce supported NaZSM-5 zeolites (Ce, 1.28×10^{-2} mmol (g-NaZSM-5)$^{-1}$; Rb : Ce atomic ratio, 4) with and without Rb at a measurement temperature of 300 (Fig. 5a) and 673 K (Fig. 5b), respectively. The amount of O_2 uptake of the pretreated Ce supported NaZSM-5 zeolites measured at 673 K, particularly the irreversible amount of O_2 uptake, was found to be considerably higher than that measured at room temperature (300 K). The addition of alkali metal to the Ce supported NaZSM-5 catalyst caused a significant increase in the amount of irreversible O_2 uptake, irrespective of the Ce supporting method. The dependence of the amount of O_2 uptake of (Rb–Ce_L)/NaZSM-5 catalyst on the Rb : Ce atomic ratio was measured at 673 K (Fig. 6). The amount of irreversible O_2 uptake increased with an increase in the Rb : Ce atomic ratio, passed through a maximum at the atomic ratio of around 4, and inversely decreased with further increase in the atomic ratio.

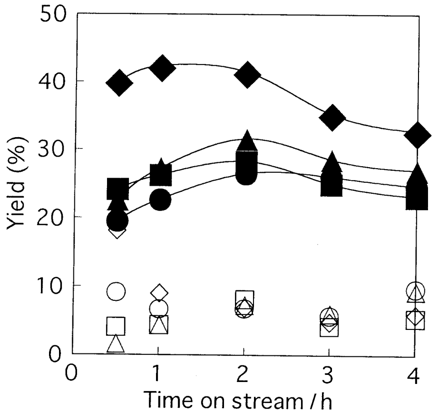

Fig. 4 Relationship between oxidation activities of various Ce and Rb supported NaZSM-5 catalysts and time on stream. Catalyst, 0.5 g; reaction temperature, 673 K; added Rb : Ce atomic ratio, 4; amount of Ce, 1.28×10^{-2} mmol (g-NaZSM-5)$^{-1}$; ◆, ◇, Ce_L/Rb/NaZSM-5; ▲, △, (Rb–Ce_L)/NaZSM-5; ■, □, Rb/Ce_L/NaZSM-5; ●, ○, Rb/Ce_L-NaZSM-5; ◆, ▲, ■, ●, yield of benzaldehyde; ◇, △, □, ○, yield of CO_2.

Oxidation activity, O_2 uptake, DR spectra, XRD patterns of high Ce impregnated NaZSM-5 catalysts with and without added alkali metal (alkali metal/Ce_H/NaZSM-5 and Ce_H/NaZSM-5) and TPO of ethanol over the alkali metal/Ce_H/NaZSM-5 and Ce_H/NaZSM-5 catalysts

To distinguish the high Ce (Ce, ~1 mmol (g-NaZSM-5)$^{-1}$) supported catalysts from the low Ce (Ce, ~10^{-2} mmol (g-NaZSM-5)$^{-1}$) supported catalysts previously described, the subscript H is added to each Ce. The influence of the alkali metal (added alkali metal : Ce atomic ratio = 0.4) added to the Ce_H/NaZSM-5 catalyst on the benzyl alcohol oxidation was investigated at the reaction temperature of 553 K (Table 4). The addition of alkali metal to the Ce_H/NaZSM-5 catalyst

Table 4 Effect of alkali metal added to Ce_H-NaZSM-5 catalyst on the yields of benzaldehyde and CO_2 [a]

Catalyst	Benzaldehyde Yield (%)	CO_2 Yield (%)
Ce_H-NaZSM-5	22.5	0.8
Li(0.4) added Ce_H/NaZSM-5	6.5	0.4
Na(0.4) added Ce_H/NaZSM-5	4.6	0.3
K(0.4) added Ce_H/NaZSM-5	3.6	0.2
Rb(0.4) added Ce_H/NaZSM-5	3.5	0.1
Cs(0.4) added Ce_H/NaZSM-5	4.8	0.2

[a] Catalyst, 0.5 g of alkali metal (0.4) impregnated Ce_H/NaZSM-5 (Si : Al atomic ratio = 58, alkali metal : Ce atomic ratio = 0.4, Ce = 2.14 mmol (g-NaZSM-5)$^{-1}$); reaction temperature, 553 K.

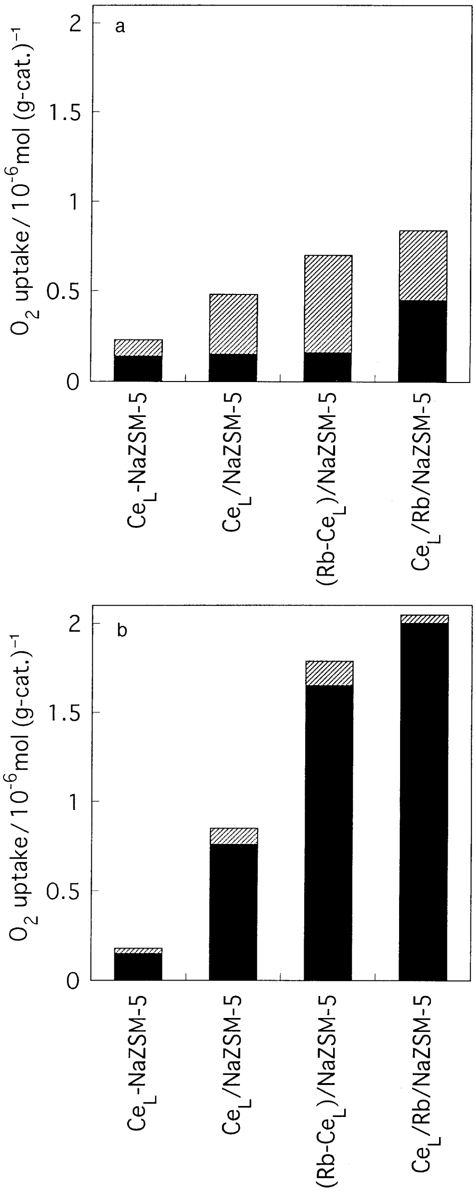

Fig. 5 Amount of O_2 uptake of prereduced Ce supported NaZSM-5 catalysts with and without Rb. Amount of Ce, 1.28 × 10^{-2} mmol (g-NaZSM-5)$^{-1}$; added Rb : Ce atomic ratio, 4; ▨, reversible O_2 uptake (see Experimental section); ■, irreversible O_2 uptake (see Experimental section); a, measured at 300 K; b, measured at 673 K.

caused the decreases in both the yields of benzaldehyde and CO_2, regardless of the type of added alkali metal. This result is in contrast with the effect of the alkali metal addition to the Ce_L/NaZSM-5 catalyst (Table 1). This suggests that the Ce species on Ce_H/NaZSM-5 are different from the corresponding ones on Ce supported NaZSM-5 (Ce_L/NaZSM-5) of which the Ce content is comparably low.

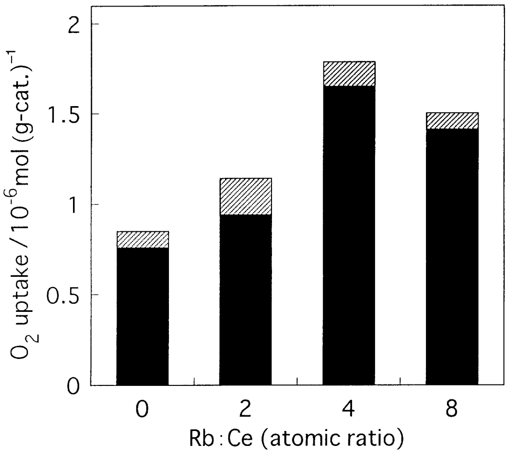

Fig. 6 Dependence of the amount of O_2 uptake on added Rb : Ce atomic ratio. Catalyst, (Rb–Ce_L)/NaZSM-5; amount of Ce, 1.28 × 10^{-2} mmol (g-NaZSM-5)$^{-1}$; temperature, 673 K; ▨, reversible O_2 uptake; ■, irreversible O_2 uptake.

After the steady-state oxidation of benzyl alcohol at 573 K over Rb added Ce_H/NaZSM-5 (Rb/Ce_H/NaZSM-5) and Ce_H/NaZSM-5 catalysts (Ce, 2.361 mmol (g-NaZSM-5)$^{-1}$; Rb, 0.927 mmol (g-NaZSM-5)$^{-1}$), both the product yields of benzaldehyde and CO_2 were followed with time on stream without a supply of gaseous O_2 (Fig. 7). First, it must be once again noted that the yield of benzyl alcohol over the Rb/Ce_H/NaZSM-5 catalyst was lower than that over Ce_H/NaZSM-5 without Rb (Fig. 7, region I), in contrast to the low Ce supported NaZSM-5 (Ce_L-, Ce_L/NaZSM-5) catalysts (Table 1) in which the amount of impregnated Cu is considerably lower (Ce, 1.28 × 10^{-2} mmol (g-NaZSM-5)$^{-1}$), as previously described. The stop of gaseous O_2 supply caused an immediate disappearance of CO_2, on the other hand, benzaldehyde formation was observed even in the absence of gaseous O_2 (region II). This detected benzaldehyde is not due to the adsorbed benzaldehyde formed during the steady-state oxidation of benzyl alcohol because the lack of supply of both O_2 and benzyl alcohol (only N_2 supply) caused no benzaldehyde formation (region V). The catalytic activities for benzaldehyde formation of the Rb/Ce_H/NaZSM-5 catalyst were found to be recovered to almost the same extent as the corresponding fresh catalysts by treating at 573 K under an air flow, though the Ce_H/NaZSM-5 catalyst tended to become deactivated by the same treatment (region IV).

The amounts of O_2 uptake of both the Rb/Ce_H/NaZSM-5 (Ce, 2.361 mmol (g-NaZSM-5)$^{-1}$; Rb 0.927 mmol (g-NaZSM-5)$^{-1}$) and Ce_H/NaZSM-5 catalysts pretreated at 773 K for 1 h under CO were compared (Fig. 8). In contrast to the result of Fig. 5(b), in which the Ce content in the Ce impregnated NaZSM-5 catalyst was less than one-hundredth of the Ce_H/NaZSM-5 catalyst, the addition of Rb to the Ce_H/NaZSM-5 catalyst caused a decrease in the amount of O_2 uptake. The values of the O_2 uptake per Ce atom between

Table 5 Effect of Ce loading on the value of O_2 uptake : Ce[a]

Catalyst	Ce loading/ mmol (g-NaZSM-5)$^{-1}$	Rb : Ce (atomic ratio)	O_2 uptake : Ce/ mol O_2 : (atom Ce)$^{-1}$
Ce_L/NaZSM-5[b]	1.28 × 10^{-2}	0	6.6 × 10^{-2}
Rb/Ce_L/NaZSM-5[b]	1.28 × 10^{-2}	4	1.4 × 10^{-1}
Ce_H/NaZSM-5[c]	2.36	0	4.4 × 10^{-2}
Rb/Ce_H/NaZSM-5[c]	2.36	0.39	3.6 × 10^{-2}

[a] Pretreatment of catalysts, see Experimental section. [b] Measurement temperature, 673 K. [c] Measurement temperature, 573 K.

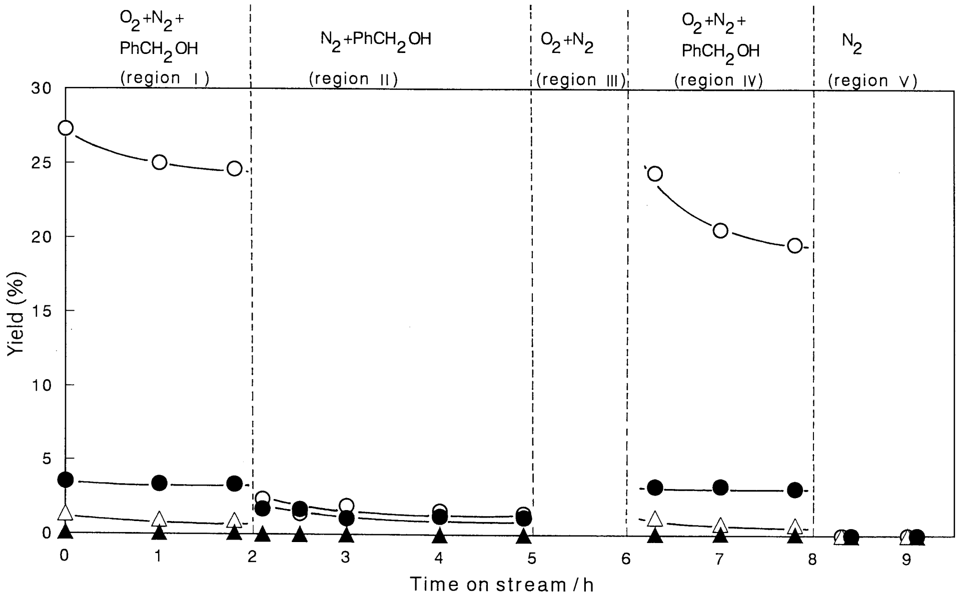

Fig. 7 Behavior of benzyl alcohol oxidation over Ce_H/NaZSM-5 catalysts with and without added Rb under a nitrogen atmosphere. Reaction temperature, 573 K; ●, ▲, Rb/Ce_H/NaZSM-5; ○, △, Ce_H/NaZSM-5; ●, ○, yield of benzaldehyde; ▲, △, yield of CO_2 ; amount of Ce, 2.36 mmol (g-NaZSM-5)$^{-1}$; amount of Rb, 0.927 mmol (g-NaZSM-5)$^{-1}$.

Ce_H/NaZSM-5 and Ce_L/NaZSM-5 catalyst, and the corresponding Rb added ones were compared, as shown in Table 5. The value of O_2 uptake : Ce of the Rb added Ce_L/NaZSM-5 catalyst was higher than that of the Ce_L/NaZSM-5 catalyst without the added Rb. In contrast, the value of O_2 uptake : Ce of Rb added Ce_H/NaZSM-5 catalyst was found to be lower than that of Ce_H/NaZSM-5 without the added Rb. The addition of Rb to both the low and high Ce impregnated NaZSM-5 catalysts worked on the value of O_2 uptake : Ce in an inverse way. Thus the Rb added to high Ce impregnated NaZSM-5, differing from the low Ce impregnated counterpart, tended to inhibit the O_2 uptake.

The DR spectra of high Ce (Ce, 3.15 and 1.57 mmol (g-NaZSM-5)$^{-1}$) impregnated NaZSM-5 catalysts (Fig. 9) were observed to study the redox behavior during oxidation and reduction treatments. (All the DR spectra were observed using high Ce impregnated catalysts because the sensitivity in the visible ray region (450–800 nm) of the Ce species in the low Ce impregnated ones was too low to be detected.) A large band was observed at 280–320 nm for all the catalysts (Fig. 9). The reduction treatment of both Ce_H/NaZSM-5 catalysts decreased the intensity (KM function) of the band at around 280–320 nm. The enlargement of the region of 450–800 nm in Fig. 9 is illustrated in Fig. 10. Neither of the preoxidized Ce_H/NaZSM-5 zeolites had a band in the 450–800 nm region. In contrast, a broad band centered around 600 nm was clearly observed in the DR spectra of the prereduced Ce_H/NaZSM-5 zeolites. The higher the content of Ce, the greater became the intensity of the broad band at around 600 nm. The effect of CO treatment (reduction) temperature on the DR spectra at 450–800 nm was investigated using the Ce_H/NaZSM-5 catalyst (Fig. 11). The decrease in the pretreatment temperature

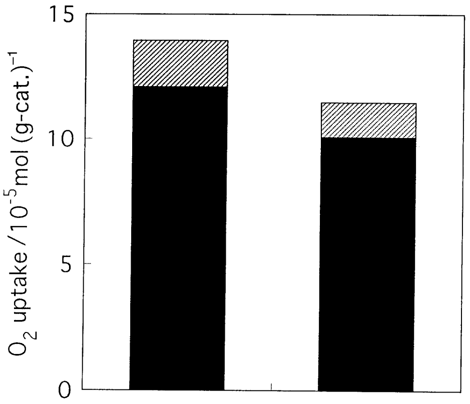

Fig. 8 Amount of O_2 uptake of Ce_H/NaZSM-5 catalysts with and without added Rb. Measured temperature, 573 K; amount of Ce, 2.36 mmol (g-NaZSM-5)$^{-1}$; amount of added Rb, 0.674 mmol (g-NaZSM-5)$^{-1}$; ▨, reversible O_2 uptake; ■, irreversible uptake.

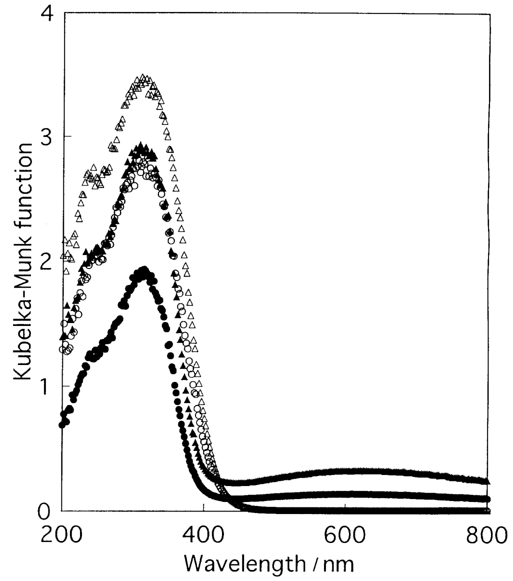

Fig. 9 DR spectra of Ce supported NaZSM-5 catalysts. △, oxidized Ce_H/NaZSM-5 (Ce, 3.15 mmol (g-NaZSM-5)$^{-1}$); ▲, reduced Ce_H/NaZSM-5 (Ce, 3.15 mmol g(NaZSM-5)$^{-1}$); ○, oxidized Ce_H/NaZSM-5 (Ce, 1.57 mmol (g-NaZSM-5)$^{-1}$); ●, reduced Ce_H/NaZSM-5 (Ce, 1.57 mmol (g-NaZSM-5)$^{-1}$); oxidation treatment, treated at 773 K for 1 h under O_2 atmosphere; reduction treatment, degassed at r.t. for 1 h and treated at 773 K for 1 h under CO atmosphere.

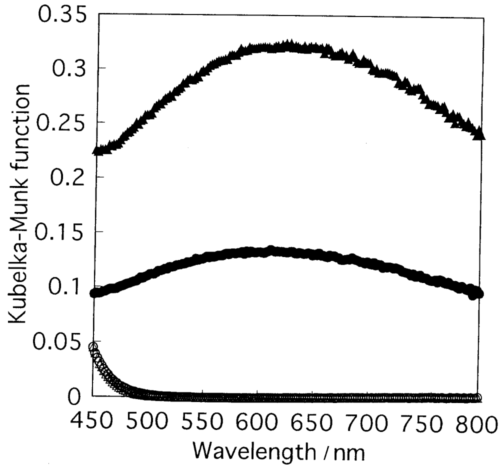

Fig. 10 DR spectra in the visible ray region of Ce supported NaZSM-5 catalysts. ▲, reduced Ce_H/NaZSM-5 (Ce, 3.15 mmol (g-NaZSM-5)$^{-1}$); ●, reduced Ce_H/NaZSM-5 (Ce, 1.57 mmol (g-NaZSM-5)$^{-1}$); △, oxidized Ce_H/NaZSM-5 (Ce, 3.15 mmol (g-NaZSM-5)$^{-1}$); ○, oxidized Ce_H/NaZSM-5 (Ce, 1.57 mmol (g-NaZSM-5)$^{-1}$); oxidation treatment, treated at 773 K for 1 h under O_2 atmosphere; reduction treatment, degassed at r.t. for 1 h and treated at 773 K for 1 h under CO atmosphere.

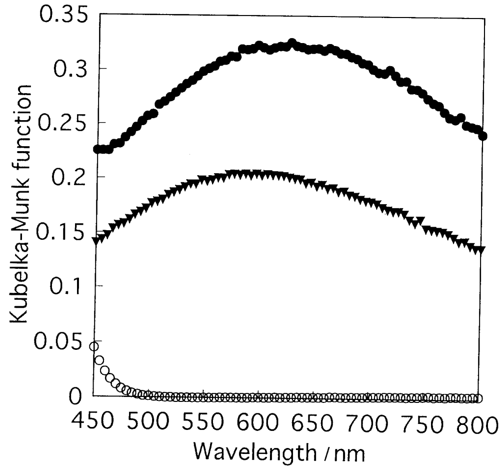

Fig. 11 Influence of reduction temperature on the DR spectra of Ce_H/NaZSM-5 catalysts. ●, Ce_H/NaZSM-5 reduced at 773 K for 1 h under CO atmosphere; ▼, Ce_H/NaZSM-5 reduced at 573 K for 1 h under CO atmosphere; ○, Ce_H/NaZSM-5 oxidized at 773 K for 1 h under O_2 atmosphere; amount of Ce, 3.15 mmol (g-NaZSM-5)$^{-1}$.

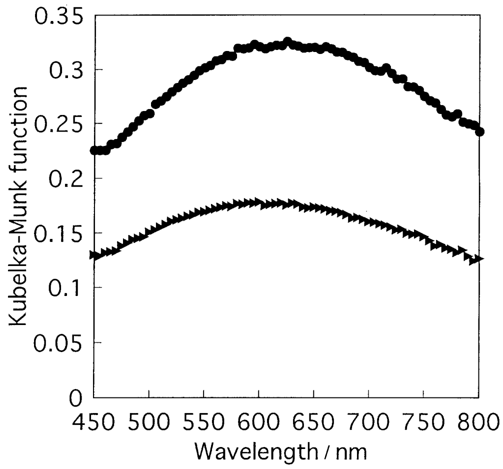

Fig. 12 Influence of added Rb on the DR spectra of Ce_H/ZSM-5 catalysts. Amount of Ce, 3.15 mmol (g-NaZSM-5)$^{-1}$; amount of added Rb, 0.899 mmol (g-NaZSM-5)$^{-1}$; ●, Ce_H/NaZSM-5 reduced at 773 K for 1 h under CO; ▼, Rb added Ce_H/NaZSM-5 reduced at 773 K for 1 h under CO.

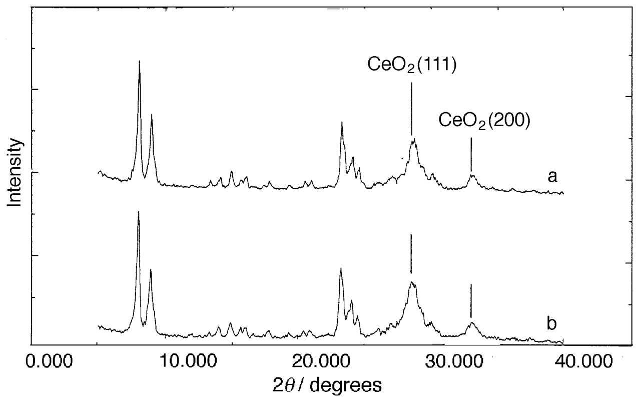

Fig. 13 XRD patterns of Ce_H/NaZSM-5 catalysts with and without added Rb. a, Ce_H/NaZSM-5; b, Rb added Ce_H/NaZSM-5; amount of Ce, 3.147 mmol (g-NaZSM-5)$^{-1}$; amount of Rb, 0.899 mmol (g-NaZSM-5)$^{-1}$.

with CO of the Ce_H/NaZSM-5 catalyst caused a decrease in the intensity of the broad band at around 600 nm. The addition of Rb to the Ce_H/NaZSM-5 catalyst pretreated with CO at 773 K was found to also decrease the intensity of the broad band at around 600 nm as illustrated in Fig. 12, though the difference in the intensity was not so great when both the Ce_H/NaZSM-5 and Rb added Ce_H/NAZSM-5 (Rb/Ce_H/NaZSM-5) catalysts were pretreated under CO at a lower temperature (573 K).

The XRD patterns of both the Ce_H/NaZSM-5 and the Rb added counterpart (Rb/Ce_H/NaZSM-5) catalysts are illustrated in Fig. 13. Two clear peaks based on CeO_2 were observed[19] at $2\theta = 28.4°$ [CeO_2 (111)] and 33.0° [CeO_2 (200)] in the XRD patterns of both catalysts. The intensities of both the peaks attributed to CeO_2 increased by the addition of Rb to the Ce_H/NaZSM-5 catalyst. (The ratio of the CeO_2 (111) peak intensity of the Rb/Ce_H/NaZSM-5 to Ce_H/NaZSM-5 was *ca.* 2.3.) The XRD patterns of the Ce_L-NaZSM-5, Ce_L/NaZSM-5 catalysts [Ce, 1.28×10^{-2} mmol (g-NaZSM-5)$^{-1}$ (Ce ion-exchange, 22%)] and both the Rb added catalysts (Rb : Ce atomic ratio, 4) showed only the pattern based on the NaZSM-5 support, but no clear peaks based on Ce species.

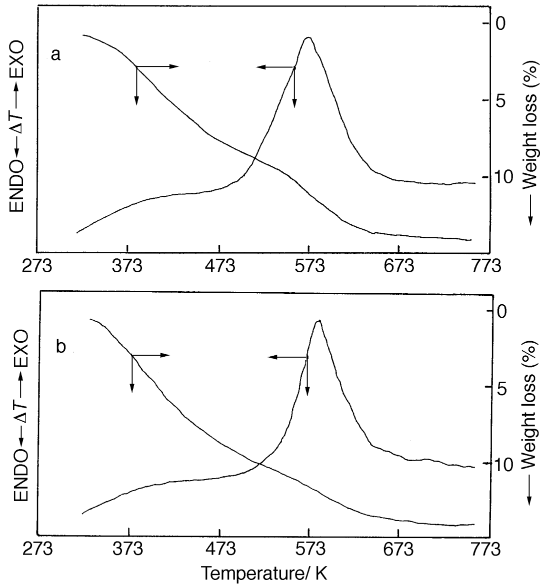

Fig. 14 TPO of ethanol over Ce_H/NaZSM-5 catalysts with and without added Rb. Amount of Ce, 3.147 mmol (g-NaZSM-5)$^{-1}$; amount of Rb, 0.899 mmol (g-NaZSM-5)$^{-1}$; a, Ce_H/NaZSM-5 catalyst; b, Rb added Ce_H/NaZSM-5 catalysts.

The TPO of ethanol was observed using the Ce_H/NaZSM-5 and the Rb added Ce_H/NaZSM-5 (Rb/Ce_H/NaZSM-5) catalysts (Ce, 3.15 mmol (g-NaZSM-5)$^{-1}$; Rb, 0.90 mmol (g-NaZSM-5)$^{-1}$), as shown in Fig. 14. Instead of benzyl alcohol, ethanol was used as a reactant because its vapor pressure is relatively low. An exothermic broad peak with weight loss was observed at 473–697 K over both catalysts. The area of the exothermic peak over the Ce_H/NaZSM-5 catalyst was calculated to be 1.38 times larger than that over the Rb/Ce_H/NaZSM-5 catalyst. Particularly the addition of Rb to the Ce_H/NaZSM-5 catalyst caused a decrease in the area of the exothermic peak at the region of lower temperature.

Discussion

Cerium species supported on NaZSM-5 zeolite were found to be active for the gas-phase catalytic oxidation of benzyl alcohol. The chemical and physical properties of Ce species on both the low Ce ion-exchanged/impregnated NaZSM-5 (Ce_L-, and Ce_L/NaZSM-5) and the high Ce impregnated NaZSM-5 (Ce_H/NaZSM-5) catalysts are discussed separately, hereafter, because the effect of alkali added to the low and high Ce supported catalysts was found, through this study, to be quite different from each other.

Low Ce supported NaZSM-5 (Ce_L-, and Ce_L/NaZSM-5) catalysts (Ce, $\sim 10^{-2}$ mmol (g-NaZSM-5)$^{-1}$) and the alkali added counterparts

The addition of alkali metal to Ce ion-exchanged (Ce_L-NaZSM-5) and/or relatively low Ce impregnated (Ce_L/NaZSM-5) zeolite catalysts was found to increase the catalytic activity for benzyl alcohol (Tables 1 and 3). Among the added alkali metals, Rb had a maximum effect for benzaldehyde formation under the present reaction conditions (Table 1). It is of interest to note that the added alkali kept the high yield of benzaldehyde and also the high selectivity for benzaldehyde at a higher reaction temperature. Thus the added alkali is considered to promote partial oxidation activity, rather than the perfect oxidation, even at high temperature. Because Rb impregnated NaZSM-5 (Rb/NaZSM-5) without Ce had only low oxidation activity, the added Rb species are suggested to be promoters for the Ce supported NaZSM-5 catalyst, rather than active species. The direct contact of the added alkali metal with active Ce species was confirmed to be important for the effective promotive role because the physical mixture of Ce_L/NaZSM-5 and Rb/NaZSM-5 did not have the same high oxidation activity as the Rb impregnated Ce_L/NaZSM-5 (Rb/Ce_L/NaZSM-5) catalyst (Table 2). The addition of too much alkali metal will cover the active Ce species followed by a decrease in the yield of benzaldehyde as evidenced from having a maximum of benzaldehyde yield at the variation of the Rb : Ce atomic ratio (Fig. 2 and 3). The oxidation results over both the Rb and Ce supported NaZSM-5 catalysts prepared by varying the supporting method and the supporting order showed that the catalyst (Ce_L/Rb/NaZSM-5) prepared (a consecutive impregnation method) by impregnating Rb followed by the impregnation of Ce had the largest oxidation activity among the prepared catalysts (Fig. 4). The results would also imply that the higher oxidation activity for the Ce_L/Rb/NaZSM-5 catalyst is due to the exposure of the active Ce species, which are promoted by the added Rb, to the outer surface.

The amount of O_2 uptake of the low Ce supported NaZSM-5 (Ce_L/NaZSM-5) catalysts, which catalysts were pretreated under CO and degassed, were found to increase by added Rb to the Ce_L/NaZSM-5 catalysts (Fig. 5a and b). The added Rb is thus supposed to promote the redox properties of Ce species supported on the NaZSM-5 through the ease of O_2 uptake and release. The greater capacity in the O_2 uptake of the Rb added catalyst than the one without Rb would contribute to benzaldehyde formation. The similar dependence between the benzaldehyde yield (Fig. 3) and the amount of O_2 uptake (Fig. 6) on the Rb : Ce atomic ratio, of which dependence both the maximum values were observed at the atomic ratio of around 4, suggests that the O_2 species sorbed on the catalyst have a strong correlation with the formation of benzaldehyde, and one of the important roles of the added alkali such as Rb is to increase the amount of the sorbed O_2 species.

High Ce impregnated NaZSM-5 (Ce_H/NaZSM-5) catalysts (Ce, ~ 1 mmol (g-NaZSM-5)$^{-1}$) and the alkali added counterparts

The addition of alkali metal to the Ce_H/NaZSM-5 catalyst decreased the yield of benzaldehyde as shown in Table 4, in contrast to the behavior of the added alkali metal to the Ce_L/NaZSM-5 catalyst (Table 3). The XRD patterns of both the Ce_H/NaZSM-5 (Ce, 3.15 mmol (g-NaZSM-5)$^{-1}$) and the Rb added counterpart clearly indicated the presence of CeO_2. However, no clear peaks based on CeO_2 were observed in the Ce_L/NaZSM-5 catalyst. The difference in the structure of the Ce species on the Ce_H/ and Ce_L/NaZSM-5 catalysts will be attributed to the reverse effect of the added alkali. The larger peaks based on the CeO_2 on the Rb added Ce_H/NaZSM-5 catalyst would suggest that the added Rb causes an increase in the size of CeO_2 particle, followed by the decrease in the benzaldehyde formation.

The reaction results (Fig. 7) that benzaldehyde was formed even in the absence of gaseous O_2, in contrast to the immediate disappearance of CO_2, indicate that the O_2 species sorbed on the Ce_H/NaZSM-5 catalyst during the steady-state oxidation are responsible for the formation of benzaldehyde. However, the enlargement of the size of the CeO_2 particle by the addition of an alkali metal such as Rb would decrease the capacity of the sorbed O_2 species. A decrease in the amount of O_2 uptake by the addition of Rb to the Ce_H/NaZSM-5 catalyst, which differed from the result of Ce_L/NaZSM-5 (Fig. 5a, b and 6), was in fact observed (Fig. 8), though the difference in the measurement temperature could not be ignored.

The DR spectra of high Ce impregnated NaZSM-5 (Ce_H/NaZSM-5) catalysts with and without the added Rb were observed under various treatment conditions to study the redox behavior of the Ce species. The large peak at 350 nm observed for bulk CeO_2 has been reported to shift to around 280 nm by supporting the Ce species on silica, and the band centered at around 280 nm has been assigned as a Ce^{IV}-oxygen charged transfer.[18] The decreases in the KM function at the bands (280–320 nm) of both Ce_H/NaZSM-5 catalysts by reduction treatment (Fig. 9) will indicate a decrease in the Ce^{IV} species in the Ce_H/NaZSM-5. The DR spectra of CeO_2 reduced at 473–973 K under H_2 have been reported to show a band at *ca.* 588 nm, which has been attributed to the reduced Ce species: $2\ CeO_2 + H_2 \rightarrow Ce_2O_3 + H_2O$.[20] The CO pretreatment of the Ce_H/NaZSM-5 catalyst caused the appearance of a broad band at around 600 nm, in contrast to no appearance of this band for the calcined Ce_H/NaZSM-5 catalyst. This will be due to the formation of reduced Ce (Ce_{red}) species by the pretreatment under CO. The increase in the broad band at around 600 nm by increases in the Ce content (Fig. 10) and/or the CO pretreatment temperature (Fig. 11) also supported that the band at *ca.* 600 nm is assigned as reduced Ce species. This variation of the DR spectra (Fig. 12) that the addition of Rb to the Ce_H/NaZSM-5 catalyst inversely brought the decrease in the intensity of the band attributed to the reduced Ce species is compatible with the decreases in both the benzaldehyde yield (Table 4) and the amount of O_2 uptake (Fig. 8) by adding Rb to the Ce_H/NaZSM-5 catalyst. The TPO of ethanol over the Rb added Ce_H/NaZSM-5 catalysts also showed a tendency to decrease the oxidation activity in comparison with the counterpart without the added Rb (Fig. 14). The Rb species added to the Ce_H/NaZSM-5 catalyst will thus cause the decrease in the amount of active O_2 species in the oxidic Ce species, of which the active O_2 species are considered to be responsible to the formation of benzaldehyde in the benzyl alcohol oxidation.

Conclusion

Low (Ce_L, $\sim 1 \times 10^{-2}$ mmol (g-NaZSM-5)$^{-1}$) and high (Ce_H, ~ 1 mmol (g-NaZSM-5)$^{-1}$) Ce supported NaZSM-5 catalysts were prepared by the ion-exchange (Ce_L-NaZSM-5) or impregnation (Ce_L/NaZSM-5, Ce_H/NaZSM-5) method, and their oxidation activities were studied using the gas-phase catalytic oxidation of benzyl alcohol. The low Ce supported NaZSM-5 catalysts (Ce_L-NaZSM-5, Ce_L/NaZSM-5) were found to increase the catalytic activity of benzaldehyde oxidation, particularly the partial oxidation activity, by adding alkali metal to the Ce_L supported NaZSM-5 catalysts, regardless of the supporting method of the Ce species. Thus, the alkali metal added to Ce_L- and Ce_L/NaZSM-5 catalysts caused the high yield of and the high selectivity for benzaldehyde. The added alkali metal such as K or Rb acted as a promoter, rather than as an active species, for the active Ce species. Too much alkali metal addition inversely caused the decrease in the benzaldehyde formation because of the covering of the alkali metal on the surface of the active Ce species. The increase in the amount of O_2 uptake of the Rb added Ce_L/NaZSM-5 catalyst prereduced with CO, in the comparison with the Ce_L/NaZSM-5 catalyst without the added Rb, suggests that an added alkali metal such as Rb has a function to increase the sorbed O_2 species which are considered to be important to benzaldehyde formation. In contrast, the addition of Rb to the high Ce impregnated NaZSM-5 (Ce_H/NaZSM-5) catalysts caused a decrease in the formation of benzaldehyde. Cerium oxide (CeO_2) species were observed in the Ce_H/NaZSM-5 catalyst. The added Rb was suggested to increase the size of CeO_2 formed on Ce_H/NaZSM-5 based on the observation of the XRD spectra of both the Ce_H/NaZSM-5 with and without the added Rb. This will make the release and/or uptake of O_2 species more difficult. In fact, the amount of O_2 uptake decreased by adding Rb to the Ce_H/NaZSM-5 catalyst prereduced with CO. The DR spectra of the Ce_H/NaZSM-5 catalyst with and without the added Rb supported the conclusion that the added Rb makes the redox property of the Ce species more difficult.

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

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