

Effect of alkali metal added to supported La catalysts on the catalytic activity in the gas-phase catalytic oxidation of benzyl alcohol

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Abstract

The oxidation activities of lanthanum (La) catalyst supported on both crystalline and amorphous oxides including NaZSM-5 zeolite and the alkali metal-added counterparts were studied using a gas-phase catalytic oxidation of benzyl alcohol. The main oxidation products were benzaldehyde and carbon dioxide, together with a trace amount of benzene and/or toluene under certain reaction conditions. The addition of alkali metal to the lanthanum catalysts supported on NaZSM-5 and SiO₂ promoted the catalytic activity of the partial oxidation in the benzyl alcohol oxidation. The influences of the oxide supports, the amount of La supported on the catalyst, the added alkali metal/La atomic ratio, and the catalyst preparation on the catalytic activity in the benzyl alcohol oxidation were investigated. The amount of adsorbed ethanol on the La-supported catalyst, the O₂ uptake amount, the transient response experiment of the oxidation reaction, together with the BET surface area and the X-ray powder diffraction (XRD) pattern of the catalysts, were measured in order to determine the crucial factors in the partial oxidation activity. A promotion scheme for the alkali metal added to the La/NaZSM-5 catalyst is proposed.

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1. Introduction

The catalytic reduction of NO_x by using some transition metal ion-exchanged ZSM-5 catalysts including Cu- and Co-ZSM-5 zeolites has been studied [1,2] to selectively remove the toxic NO_x exhausted from a variety of combustion engines. The application of lanthanum, as an additive, has been reported [3,4] to inhibit the de-alumination of the Cu or Co supported ZSM-5 catalyst during the selective catalytic reduction of NO_x and to prolong the lifetime of these catalysts. The introduction of both alkali metal oxide and lanthanum oxide (La₂O₃) into a nickel oxide catalyst supported on alumina was reported [5] to improve the activity and the thermal stability of the catalyst for the partial oxidation of methane to syngas and also to inhibit the carbon deposit over the supported nickel species.

In the study on the development of the supported Cu catalysts being active for the partial oxidation in the gas-phase

catalytic oxidation of benzyl alcohol, the addition of alkali metal to the supported Cu catalysts have been reported [6–12] to be effective, and the role of the added alkali metal has also been discussed. A cerium catalyst supported on NaZSM-5 zeolite and the alkali metal-added counterpart was also applied [13,14] to the catalyst for the gas-phase catalytic oxidation of benzyl alcohol. A Cu complex with a 14-membered macrocyclic dioxotetramine ligand has been reported to catalyze the liquid-phase oxidation of benzyl alcohol to benzaldehyde at room temperature and to be regarded as a mimic for galactose oxidase [15]. A polymer-bound Ru Schiff base complex has been used in the liquid-phase oxidation of benzyl alcohol [16]. Kaneda and coworkers have reported [17–19] highly effective Ru³⁺ incorporated hydroxyapatite and hydrotalcite catalysts for the liquid-phase oxidation of alcohols including benzyl alcohol with O₂ as the oxidant.

In extending the study on the application of alkali metal as a promoter for the supported metal catalysts in the gas-phase catalytic oxidation of benzyl alcohol, the partial oxidation activity of both the lanthanum catalysts supported on NaZSM-5 (La/NaZSM-5) zeolite and the alkali

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metal-added counterparts was investigated using the titled reaction. The alkali metal added to the supported La catalysts caused selective promotion of the catalytic activity for the partial oxidation.

2. Experimental

2.1. Catalysts

NaZSM-5 zeolite was prepared in this lab according to a patent [20]. The synthesized ZSM-5 zeolite was twice treated with an aqueous solution including 1 M NaNO₃ at 343–358 K to obtain NaZSM-5 ion-exchanged with 100% Na cation. The NaZSM-5 zeolite was dried at 383 K overnight and calcined at 773 K for 5 h in flowing air. The Si/Al atomic ratio of the NaZSM-5 zeolite was determined by an atomic absorption spectrometer (Shimadzu Type AA-630-01) after the zeolite was homogeneously dissolved using a few drops of hydrogen fluoride solution (Stera Chemicals, guaranteed reagent, 47%). NaX (Tosoh, Si/Al = 1.25), NaY (Tosoh, Si/Al = 2.5), and NaA (Union-Showa) zeolites were treated twice with a 1 M NaNO₃ aqueous solution at 343–358 K. All the zeolites were dried at 383 K overnight and calcined at 773 K for 5 h in flowing air. The La-supported catalysts were prepared by a conventional impregnation method using an aqueous solution including La(CH₃COO)₃·1.5H₂O (Nacalai Tesque, guaranteed reagent). The La-supported catalysts (La/zeolite) were dried at 393 K overnight and calcined at 773 K for 5 h in flowing air. The alkali metal-added La/zeolites were prepared by impregnating the alkali metal acetate on the corresponding La/zeolites. The resultant alkali metal/La/zeolite was dried at 393 K overnight and calcined at 773 K for 3 h in flowing air.

2.2. Gas-phase catalytic oxidation of benzyl alcohol

Benzyl alcohol (Nacalai Tesque, guaranteed reagent) was used as received after examining by gas chromatography (GLC). The oxygen and nitrogen gases (Kobe Oxygen Co.) were used after drying through a silica gel column. The gas-phase catalytic oxidation of benzyl alcohol was carried out at atmospheric pressure in a continuous flow fixed-bed reactor made from Pyrex glass (i.d. 15 mm). The catalyst (usually 0.5 g) placed in the reactor was pre-calcined at 773 K for 2 h in flowing air. The oxidation reaction was started by feeding benzyl alcohol in a micro-feeder. The typical reaction conditions are as follows: $W/F = 21.7 \text{ g}_{\text{cat}} \text{ min/mol}$; W (catalyst weight) = 0.5 g; F (total molar flow) = 0.023 mol/min; N₂:O₂:benzyl alcohol = 32:3:1 (mole ratio). The liquid product and the unreacted benzyl alcohol were trapped and collected using a refrigerant (diethyl malonate + liquid N₂, 223 K). The obtained sample diluted with 1 ml dimethylformamide as an internal standard was analyzed using a GLC (Shimadzu Type GC-8A) equipped with a FID using a 2 m glass column packed with PEG

HIT (5%) on Uniport HP (60/80 mesh) at 373–473 K (programmed rate, 20 K/min) under an N₂ carrier. The gaseous products were analyzed by the intermediate cell method [21] with a GLC (Shimadzu Type GC-8A) equipped with a TCD using stainless steel columns containing silica gel (1 m) and 5A molecular sieves (1 m) at 393 and 293 K, respectively, under a H₂ carrier. The conversion, the yield and the selectivity of each product were defined [14] as follows: Conversion of benzyl alcohol (%) = $\{([\text{moles of benzaldehyde produced}] + (1/7)[\text{moles of CO}_2 \text{ formed}]) / [\text{moles of benzyl alcohol fed}]\} \times 100$; yield of benzaldehyde (%) = $\{([\text{moles of benzaldehyde produced}] / [\text{moles of benzyl alcohol fed}]) \times 100\}$; yield of CO₂ ($\{(1/7)[\text{moles of CO}_2 \text{ produced}] / [\text{moles of benzyl alcohol fed}]\} \times 100$); selectivity of benzaldehyde (%) = $\{([\text{moles of benzaldehyde produced}] / ([\text{moles of benzaldehyde produced}] + (1/7)[\text{moles of CO}_2 \text{ formed}])\} \times 100$; selectivity of CO₂ (%) = $\{([\text{moles of CO}_2 \text{ produced}] / ([\text{moles of benzaldehyde produced}] + (1/7)[\text{moles of CO}_2 \text{ formed}])\} \times 100$. Where [-] is the number of moles produced or fed. The obtained carbon balances in this study were more than 90%, although the carbon balance over the La catalysts supported on NaA and NaX was around 80%.

2.3. Measurement of BET surface area

The surface areas of the catalysts were measured by the BET method based on the nitrogen adsorption at 77 K in a micro-adsorption vacuum apparatus (residual pressure below 10⁻³ Pa).

2.4. Measurement of X-ray diffraction (XRD) profiles

The X-ray powder diffraction (XRD) patterns were recorded in a Rigaku RINT 2001 XRD diffractometer using the Cu K α line at room temperature.

2.5. Measurement of the amount of O₂ uptake

The amount of O₂ uptake of the pre-reduced La-supported catalysts was measured using a semi-micro gas-absorption equipment with a capillary glass sample tube. A 0.2 g catalyst sample was degassed at room temperature for 30 min followed by calcining at 773 K for 1 h with 20 kPa O₂. After degassing at room temperature for 30 min, the sample was treated at 773 K for 1 h with 20 kPa CO followed by degassing at a specified temperature. The dead volume was obtained by measuring the equilibrium pressure after introducing 1.3 kPa He. The total amount of O₂ uptake was obtained by measuring the equilibrium pressure after introducing 5.2 kPa O₂. After degassing for 1 h followed by once again introducing 5.2 kPa O₂, the reversible amount of O₂ uptake was obtained in the same way. The irreversible amount of O₂ uptake was estimated by subtracting the reversible amount of O₂ uptake from the corresponding total amount.

2.6. Measurement of the amount of ethanol adsorption on the catalyst

The amount of ethanol adsorption on the supported La catalysts was obtained using a thermal gravimetric analysis (TGA–DTA) unit (Shimadzu Type DTG-40). The catalyst (0.05 g) set in the TGA cell was calcined at 773 K for 1 h in flowing air (30 ml/min). The catalyst was purged in N₂ flow (100 ml/min) at 293 K (or 308 K) for 15 min. Ethanol (0.15 vol.%) in N₂ was then continuously introduced to the supported La catalyst at 293 K (or 308 K) to measure the weight of adsorbed ethanol.

3. Results and discussion

No oxidation products were detected and the starting material, benzyl alcohol, was quantitatively recovered when the gas-phase oxidation of benzyl alcohol was attempted at 653 K using only quartz sand, a diluent for the catalyst. Main oxidation products over the supported La catalysts were benzaldehyde and carbon dioxide. Only traces of benzene and/or toluene were detected depending on the reaction conditions. The yield of the oxidation product was usually estimated as the average of the three yields obtained at the times on stream of 2, 3, and 4 h.

3.1. Influence of the catalyst support on the oxidation activity

The gas-phase catalytic oxidation of benzyl alcohol was performed over the supported La (3.0 wt.%) catalysts (Table 1). All the supports themselves were also attempted as the catalysts for the oxidation. Except for the La/NaA catalyst, the supported La catalysts studied here had the higher yield of benzaldehyde than those over the supports themselves, though the increases in the yield of benzaldehyde were not significant. The partial oxidation activity decreased by supporting lanthanum on NaA zeolite, different from the other oxide supports. The XRD patterns of both the NaA and La(3.0)/NaA (La, 3.0 wt.%) zeolites

Table 1
Influence of the support on the oxidation activity^a

Catalyst	Benzaldehyde		CO ₂ yield (%)
	Yield (%)	Selectivity (%)	
NaZSM-5	1.3	71.8	0.51
La(3.0)/NaZSM-5	1.9	83.3	0.38
NaA	3.2	97.0	0.1
La(3.0)/NaA	1.0	90.9	0.1
NaX	0.9	18.8	4.1
La(3.0)/NaX	2.3	37.1	3.9
SiO ₂	1.4	87.5	0.2
La(3.0)/SiO ₂	5.0	86.2	0.8

^a Catalyst, 0.5 g; La loading, 3.0 wt.%; reaction temperature, 653 K.

Table 2
BET surface area of La-supported NaA and NaZSM-5 and Rb-added counterparts^a

Catalyst	BET surface area (m ² /g)
NaZSM-5	328
La(3.0)/NaZSM-5	312
Rb(4)/La(3.0)/NaZSM-5	244
NaA	135
La(3.0)/NaA	31
Rb(4)/La(3.0)/NaA	25

^a Supported La, 3.0 wt.%.

showed no difference and were typical due to the NaA zeolite though the peak intensity of the latter tended to become smaller than that of the former. The BET surface area of the NaA was compared with the La(3.0)/NaA, together with the data of both the NaZSM-5 and the La(3.0)/NaZSM-5 zeolites (Table 2). The impregnation of 3.0 wt.% La on the NaZSM-5 support exerted little influence on the BET surface area, but the BET surface area of the La(3.0)/NaA catalyst significantly declined, compared with that of the NaA support itself. The lower yield of benzaldehyde over the La/NaA zeolite than over the NaA may be due to the striking decrease in the BET surface area by impregnating lanthanum on the A type zeolite with smaller pores.

The effect of the alkali metal added to the supported La catalyst on the yield of benzaldehyde was investigated using rubidium (Table 3). The atomic ratio of the added Rb/La was maintained at a constant 4. Except for the Rb(4)/La(3.0)/NaA (added Rb/La, 4; La, 3.0 wt.%) catalyst, the addition of Rb to the supported La catalysts caused an increase in the yield of benzaldehyde; particularly the selectivity for benzaldehyde, together with the yield of benzaldehyde, significantly increased over both the Rb(4)/La(3.0)/NaZSM-5 and the Rb(4)/La(3.0)/SiO₂ catalysts. This result indicates that the promotion effect of the added alkali metal less likely depend on the crystallinity of the oxide support. The added Rb was found to selectively promote the partial oxidation of benzyl alcohol of the supported La catalysts. The La catalyst supported on NaZSM-5 and the alkali metal added counterparts were investigated in detail hereafter.

Table 3
Influence of the rubidium added to supported La catalysts on the oxidation activity^a

Catalyst	Benzaldehyde		CO ₂ yield (%)
	Yield (%)	Selectivity (%)	
Rb(4)/La(3.0)/NaZSM-5	22.3	98.8	0.28
Rb(4)/La(3.0)/NaA	0.67	79.8	0.12
Rb(4)/La(3.0)/NaX	4.57	59.6	3.1
Rb(4)/La(3.0)/SiO ₂	20.0	98.8	0.25

^a Catalyst, 0.5 g; La loading, 3.0 wt.%; added Rb/La atomic ratio, 4; reaction temperature, 653 K.

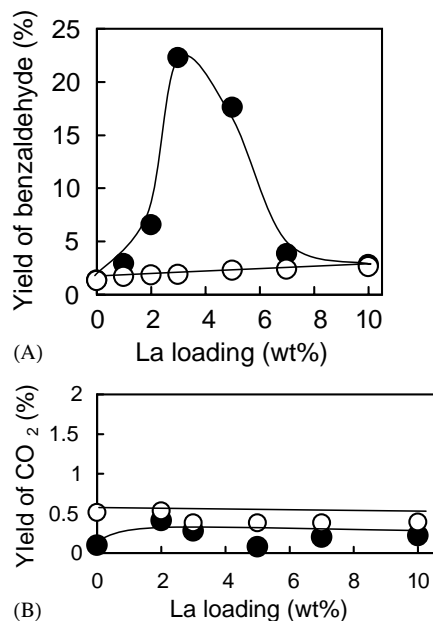


Fig. 1. Dependence of the La loading of the La/NaZSM-5 and Rb(4)/La/NaZSM-5 catalysts on the oxidation activity. Catalyst: (○) La/NaZSM-5, (●) Rb(4)/La/NaZSM-5 (Rb/La atomic ratio = 4); catalyst amount, 0.5 g; reaction temperature, 653 K. (A) Yield of benzaldehyde; (B) yield of CO₂.

3.2. Dependence of the amount of supported La on the oxidation activity

The dependence of the amount of supported La of the Rb(4)/La/NaZSM-5 (added Rb/La atomic ratio, 4) catalysts on the oxidation activity was investigated under a constant amount of the added Rb/La atomic ratio of 4 (Fig. 1A and B). The catalytic activity of the La/NaZSM-5 catalyst without the added Rb was also examined to clarify the influence of the added Rb. While the yield of benzaldehyde did not vary with an increase in the amount of the supported La over the La/NaZSM-5 catalyst without the added Rb (Fig. 1A, ○), the yield of benzaldehyde over the Rb(4)/La/NaZSM-5 catalyst significantly increased with the increasing La amount and reached maximum at around the amount of 3 wt.% of supported La, but a further increase in the supported La caused a sharp decline in the yield of benzaldehyde (Fig. 1A, ●). The yields of CO₂ over both the La/NaZSM-5 catalysts and the Rb-added counterparts were almost independent of the amount of the supported La and were considerably low in the range of the amount of La studied here (Fig. 1B, ●, ○). In order to examine the cause of the decrease in the partial oxidation activity of the Rb(4)/La/NaZSM-5 catalyst with a large amount of supported La, the dependence of the yield of benzaldehyde on the time on stream was observed using both the Rb(4)/La(3)/NaZSM-5 and the Rb(4)/La(10)/NaZSM-5 catalysts (Fig. 2). The yield of benzaldehyde over the Rb(4)/La(3)/NaZSM-5 catalyst was almost constant and no deactivation was observed. In contrast, the yield of

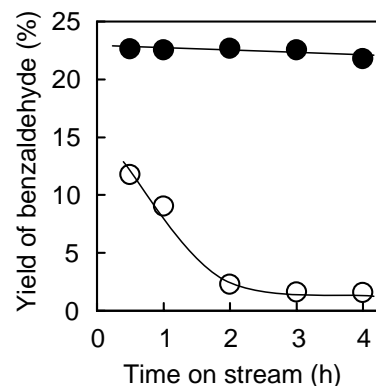


Fig. 2. Dependence of the yield of benzaldehyde over the Rb(4)/La(3.0)/NaZSM-5 and the Rb(4)/La(10)/NaZSM-5 catalysts on the time on stream. Catalyst: (○) Rb(4)/La(10)/NaZSM-5 (Rb/La atomic ratio = 4, La = 10 wt.%), (●) Rb(4)/La(3.0)/NaZSM-5 (Rb/La atomic ratio = 4, La = 3.0 wt.%); catalyst amount, 0.5 g; reaction temperature, 653 K.

benzaldehyde over the Rb(4)/La(10)/NaZSM-5 catalyst decreased with the increase in the time on stream. The XRD pattern at $2\theta = 5\text{--}30^\circ$ (Fig. 3) of the fresh Rb(4)/La(3)/NaZSM-5 catalyst indicated the XRD pattern characteristic to NaZSM-5 support, though the intensity was smaller than that of the NaZSM-5 itself. However, the corresponding XRD pattern of the fresh Rb(4)/La(10)/NaZSM-5 catalyst almost completely disappeared, meaning the destruction of the crystalline structure of the ZSM-5 type zeolite. The visual observation of the used Rb(4)/La(10)/NaZSM-5 catalyst showed a color change in the catalyst from white to black, indicating a deposit of carbonaceous materials on the catalyst. The obtained results suggest that a large amount of the supported La, with the added Rb at four times the La destroys the regular pore structure of the ZSM-5 zeolite, the structure of which prevents the deposition of carbon-like materials followed by sustainability of the catalytic activity.

3.3. Dependence of the amount of the added alkali metal/La atomic ratio on the oxidation activity

The dependence of the added alkali metal/La atomic ratio on the oxidation activity was investigated at the reaction tem-

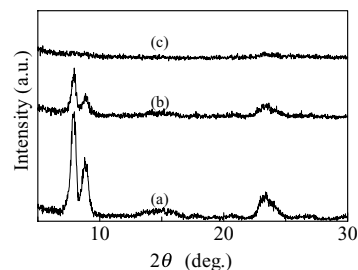


Fig. 3. XRD patterns of La/NaZSM-4 catalysts with and without added Rb. All samples were pretreated at 773 K for 3 h in flowing air: (a) NaZSM-5 support; (b) Rb(4)/La(3.0)/NaZSM-5; (c) Rb(4)/La(10)/NaZSM-5.

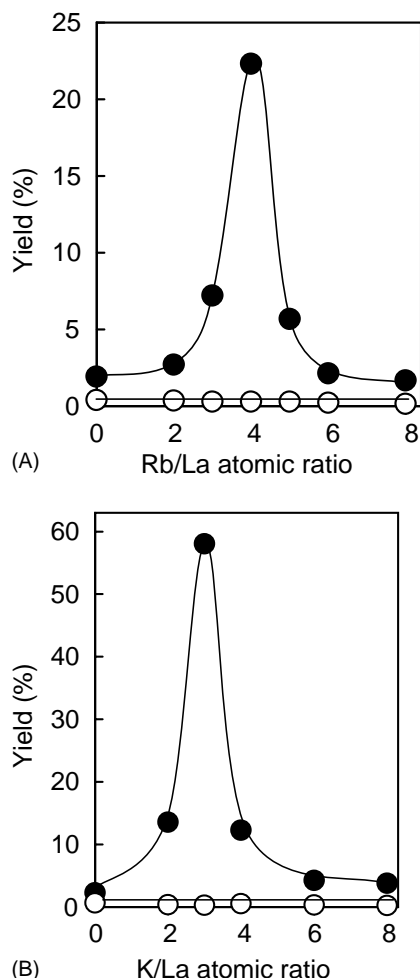


Fig. 4. Influence of the added alkali metal/La atomic ratio on the oxidation activity. Catalyst, 0.5 g; reaction time, 653 K; (○) yield of CO₂; (●) yield of benzaldehyde. (A) Rb/La(3.0)/NaZSM-5 catalyst; (B) K/La(3.0)/NaZSM-5 catalyst.

perature of 653 K using the Rb/La(3.0)/NaZSM-5 and the K/La(3.0)/NaZSM-5 catalysts (Fig. 4A and B). The yields of benzaldehyde over both the Rb/La(3.0)/NaZSM-5 and the K/La(3.0)/NaZSM-5 catalysts significantly increased with the increasing of the added alkali metal/La atomic ratio, passed through a maximum at an atomic ratio of around 4 (Fig. 4A) and 3 (Fig. 4B) and decreased at atomic ratios of more than around 4 and 3, respectively. The yield of CO₂ was almost constant and maintained low values, irrespective of the added alkali metal/La atomic ratios. An adequate amount of alkali metal added to the La/NaZSM-5 was confirmed to selectively promote the partial oxidation of benzyl alcohol.

3.4. Effect of the added alkali metal on the oxidation activity

The effect of the added alkali metal was examined using Li, Na, K, Rb, and Cs salts as the additive to the

Table 4
Effect of the added alkali metal on the oxidation activity^a

Catalyst	Benzaldehyde		CO ₂ yield (%)
	Yield (%)	Selectivity (%)	
La(3.0)/NaZSM-5	1.9	83.3	0.38
Li(4)/La(3.0)/NaZSM-5	4.5	80.9	1.06
Na(4)/La(3.0)/NaZSM-5	19.6	98.0	0.40
K(4)/La(3.0)/NaZSM-5	5.3	96.7	0.18
Rb(4)/La(3.0)/NaZSM-5	22.3	98.8	0.28
Cs(4)/La(3.0)/NaZSM-5	9.4	98.2	0.17

^a Catalyst, 0.5 g; La loading, 3.0 wt.%; added Rb/La atomic ratio, 4; reaction temperature, 653 K.

La(3.0)/NaZSM-5 catalyst (Table 4). The added alkali metal/La atomic ratio was kept at a constant 4. All the alkali metals were found to promote the catalytic activity for the partial oxidation, though the selectivity for benzaldehyde decreased on using the Li-added counterpart, compared with that over the La(3.0)/NaZSM-5 catalyst without the added alkali metal. Both Na and Rb among the added alkali metals under the condition of an added-alkali metal/La atomic ratio of 4 were notably effective as the promoter for the catalytic activity of the partial oxidation. As seen in Fig. 3a and b, the optimum value of the added alkali metal/La atomic ratio for the partial oxidation activity is thought to differ with every alkali metal, though we did not attempt to obtain an optimum atomic ratio for all alkali metals.

3.5. Influence of the preparation method of the Rb added La/NaZSM-5 catalyst on the oxidation activity

Because the alkali metal was ascertained to promote the oxidation activity of the supported La, the influence of the interaction between the active site, La and the promoter, Rb was examined using catalysts including both La and Rb prepared by different methods (Table 5). The yield of benzaldehyde of the only-Rb-supported NaZSM-5 (Rb/NaZSM-5) catalyst was low and almost the same as that of the NaZSM-5 support. The order of the impregnation of the La and Rb was found to affect the yield of benzaldehyde. The result in which the Rb(4)/La(3.0)/NaZSM-5 catalyst, which was first impregnated with La followed by impregnation with Rb, had a higher catalytic activity than the La(3.0)/Rb(4)/NaZSM-5 catalyst, the impregnation order of which is opposite to that of the Rb(4)/La(3.0)/NaZSM-5 catalyst, may demonstrate that benzyl alcohol is initially activated by the added Rb followed by being oxidized on the La site. The comparatively low yield of benzaldehyde over the catalyst prepared by co-impregnation, compared with the catalysts prepared by consecutive impregnation, may suggest that the relatively larger La particle is effective for benzaldehyde formation. The physically mixed catalytic systems (La(3.0)/NaZSM-5 + Rb/NaZSM-5 and La(3.0)/NaZSM-5 + K/NaZSM-5) gave a higher yield of benzaldehyde than that over the La(3.0)/NaZSM-5 catalyst without the added Rb or K, but the yields were significantly

Table 5
Influence of the preparation method on the oxidation activity^a

Catalyst	Benzaldehyde		CO ₂ yield (%)
	Selectivity (%)	Yield (%)	
NaZSM-5	1.3	71.8	0.51
La(3.0)/NaZSM-5	1.9	83.3	0.38
Rb/NaZSM-5 ^b	1.4	93.3	0.10
Rb(4)/La(3.0)/NaZSM-5	22.3	98.6	0.28
La(3.0)/Rb(4)/NaZSM-5 ^c	14.2	99.2	0.11
Rb(4)-La(3.0)/NaZSM-5 ^d	9.0	97.5	0.23
La(3.0)/NaZSM-5 + Rb/NaZSM-5 ^e	4.0	86.4	0.63
K(3)/La(3.0)/NaZSM-5	58.0	99.3	0.40
La(3.0)/NaZSM-5 + K/NaZSM-5 ^e	9.6	96.0	0.40

^a Catalyst, 0.5 g; La loading, 3.0 wt.%; added Rb/La atomic ratio, 4; reaction temperature, 653 K.

^b Rb amount, same as that added to the Rb(4)/La(3.0)/NaZSM-5 catalyst.

^c Rb was first impregnated followed by impregnating La.

^d La and Rb were co-impregnated.

^e The La(3.0)/NaZSM-5 and the Rb/NaZSM-5 or K/NaZSM-5 were physically mixed. The amount of Rb or K in the Rb/or K/NaZSM-5 was the same as that of the Rb(4)/La(3.0)/NaZSM-5 catalyst.

lower than those over the Rb(4)/La(3.0)/NaZSM-5 and the K(4)/La(3.0)/NaZSM-5 catalysts. This result indicates that the alkali metal present as the nearest neighbor of the La species, rather than spatially apart from the La, effectively functions as a promoter for the partial oxidation.

3.6. Dependence of reaction temperature on the oxidation activity

The dependence of the reaction temperature on the oxidation activity was investigated using the K(3)/La(3.0)/NaZSM-5 catalyst. (Table 6) High reaction temperature brought about the high yield of benzaldehyde, but the yield of CO₂ was considerably low even at the high reaction temperature, though the degree of increase of the yield of CO₂ was larger than that of benzaldehyde. The addition of alkali metal to the La/NaZSM-5 catalyst was thus found to give the yield of the benzaldehyde while retaining a high selectivity for benzaldehyde at higher reaction temperature.

3.7. Interaction of O₂ with the La/NaZSM-5 catalyst and the Rb-added counterpart

The amount of O₂ uptake of the La(3.0)/NaZSM-5 catalyst, and the Rb(4)/La(3.0)/NaZSM-5 and the K(4)/La(3.0)/

Table 6
Dependence of the reaction temperature on the oxidation activity^a

Reaction temperature (K)	Yield of benzaldehyde (%)	Selectivity of benzaldehyde (%)	Yield of CO ₂ (%)
603	29.8	99.5	0.14
653	58.0	99.3	0.40
703	77.1	97.8	1.76

^a Catalyst, 0.5 g of K(3)/La(3.0)/NaZSM-5 (La loading, 3.0 wt.%; K/La atomic ratio = 3).

NaZSM-5 catalysts was measured after these catalysts was treated with CO at 773 K for 1 h (see Section 2.5). However, the amounts of O₂ uptake of both the pre-treated catalysts were negligible within error limits. This result indicates that the La species, irrespective of the presence of alkali metal, has no redox property, differing from the Cu [8,10,11] and Ce [13] supported NaZSM-5 catalysts. This may not be surprising because the La species thought to be supported as La³⁺ (La₂O₃) in the present condition are sufficiently stable with the electronic configuration of a Xe core, 4f⁰. For the La(3.0)/NaZSM-5, the Rb(4)/La(3.0)/NaZSM-5 and the K(3)/La(3.0)/NaZSM-5 catalysts, a series of transient response experiments were conducted in which, once steady state had been achieved, the supply of O₂ was halted. In the absence of O₂, the formation of benzaldehyde and CO₂ stopped. One of the possible interpretations of the results is that in the La catalyst supported on NaZSM-5, gaseous oxygen contributes to the formation of benzaldehyde, rather than the adsorbed oxygen species as observed in the supported Cu catalyst [8,10,11] and the supported Ce catalysts [13], though the participation of the adsorbed oxygen species do not deny if the adsorbed oxygen species were thought to be too active and short-lived intermediates.

3.8. Adsorption of ethanol on the La/NaZSM-5 and the Rb/La/NaZSM-5 catalysts

The adsorption capabilities at room temperature (293 K) of both the La(3.0)/NaZSM-5 catalyst, and the Rb(4)/La(3.0)/NaZSM-5 and K(3)/La(3.0)/NaZSM-5 catalysts were compared using gaseous ethanol as an adsorbate, in place of benzyl alcohol because of its comparatively low boiling point. The adsorption amounts of ethanol on these catalysts are tabulated in Table 7, together with the adsorption amounts on the NaZSM-5 support and the Rb/NaZSM-5. The adsorption amount of ethanol on the Rb(4)/La(3.0)/NaZSM-5 and the K(3)/La(3.0)/NaZSM-5 catalysts, in addition to the Rb/NaZSM-5 and the K/NaZSM-5, was higher than that adsorbed on the La/NaZSM-5 catalyst. The adsorption amounts of ethanol over the Rb- and K/La/NaZSM-5 catalysts and the corresponding

Table 7
Adsorption amount of ethanol^a

Catalyst ^b	Adsorption amount of ethanol (mmol/g _{cat})
NaZSM-5	0.082
La(3.0)/NaZSM-5 ^b	0.085
Rb/NaZSM-5 ^c	1.06
Rb(4)/La(3.0)/NaZSM-5 ^b	0.92
K/NaZSM-5 ^c	1.69
K(3)/La(3.0)/NaZSM-5 ^b	2.04

^a Catalyst, 0.5 g; adsorption temperature, 293 K.

^b La loading, 3.0 wt.%; added Rb/La and added K/La atomic ratios, 4 and 3, respectively.

^c Rb and K amount, same as that added to the Rb(4)/La(3.0)/NaZSM-5 catalyst.

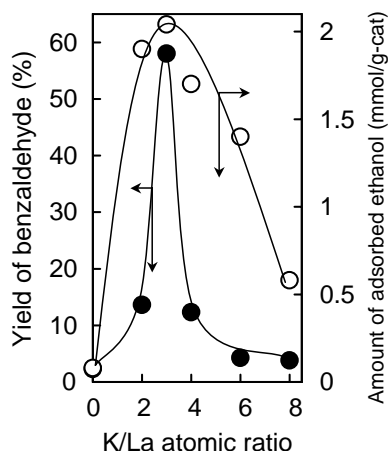
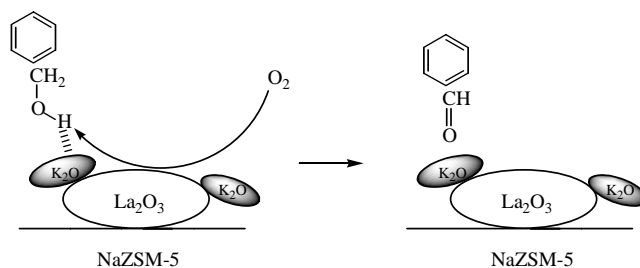


Fig. 5. Variation of the amount of adsorbed ethanol on the added K/La atomic ratio of the K/La/NaZSM-5 catalyst. Catalyst, 0.5 g; reaction time, 653 K; (○) amount of adsorbed ethanol; (●) yield of benzaldehyde.

Rb- and K/NaZSM-5 zeolites were substantially similar. However, as shown in Table 1, the catalytic activity of the Rb/NaZSM-5 for the partial oxidation of benzyl alcohol was considerably lower than that of the Rb/La/NaZSM-5 catalyst. This result clearly indicates that the partial oxidation of benzyl alcohol needs La oxide as active species, in addition to the added alkali metal which promotes the adsorption of an alcohol molecule. One of the roles of the added Rb may be to promote the adsorption of benzyl alcohol followed by activating and effecting the oxidation of the alcohol more readily, as discussed previously. The variation in the amount of ethanol adsorbed on the K/La/NaZSM-5 catalyst with different added K/La atomic ratios was investigated under the condition of a constant amount of impregnated La species (Fig. 5). The variation in the yield of benzaldehyde relative to the K/La atomic ratio is also depicted in order to compare the variation in both the amount of adsorbed ethanol and the yield of benzaldehyde. The amount of adsorbed ethanol increased with the increasing K/La atomic ratio, passed through a maximum at an atomic ratio of around 3, and inversely decreased with a further increase in the K/La atomic ratio, in agreement with the behavior of the yield of benzaldehyde, although the shapes of both variations are different in a more detailed comparison. These results suggest that the differences in the cross-sectional area and the inductive effect of both the alcohols cause the difference in the trend Fig. 4 and/or factors other than the activation of alcohol reagent by adsorption on the added alkali metal are functioning in the formation of benzaldehyde.

3.9. A plausible promotion scheme of added alkali metal on the La/ZSM-5 catalyst

From the results obtained in this study, the alkali metal added to the La/ZSM-5 catalyst was found to selectively



Scheme 1.

promote the formation of benzaldehyde. A plausible promotion scheme of the alkali metal added to the La/NaZSM-5 catalyst is illustrated in Scheme 1, based on the results obtained. The added alkali metal located in the vicinity of the supported La oxide will be useful for the promotion of benzaldehyde because the oxidation activity over a physical mixture of alkali metal/NaZSM-5 and La/NaZSM-5 is lower than that over the alkali metal/La/NaZSM-5 catalyst (Table 5). Gaseous oxygen, rather than the adsorbed oxygen species, will directly participate the formation of benzaldehyde because benzaldehyde was hardly detected in the absence of gaseous oxygen. In the beginning, benzyl alcohol will interact with the added alkali metal to be activated. The activated benzyl alcohol will be oxidized by the gaseous oxygen interacted with the supported La_2O_3 , though we have no experimental evidence for the interaction between O_2 and La_2O_3 . The supported La oxide may activate the gaseous O_2 for the partial oxidation activity because the alkali metal-supported NaZSM-5 without La oxide had only a low activity for the partial oxidation.

4. Conclusions

The catalytic activities of the lanthanum (La) catalysts supported on the zeolite and SiO_2 (La/support) and the alkali metal-added counterparts (alkali metal/La/support) were studied using the gas-phase catalytic oxidation of benzyl alcohol. The addition of alkali metal to the La/NaZSM-5 and La/ SiO_2 catalysts caused an increase in the oxidation activity, particularly the partial oxidation activity of benzyl alcohol. The amount of the added alkali metal had an optimal value relative to a constant amount of the supported La for the activity of the partial oxidation. The catalytic system in which the La/NaZSM-5 and the Rb/NaZSM-5 (or K/NaZSM-5) were physically mixed had a considerably lower catalytic activity for the partial oxidation than the Rb/La/NaZSM-5 catalyst. The close proximity of the added alkali metal to the supported La species was suggested to be necessary for the promotion effect of the added alkali metal. The added alkali metal was indicated to play an important role in activating the reactant through the adsorption of benzyl alcohol, in addition to inhibiting the deposition of carbonaceous materials on the catalyst. The promotion function

of the alkali metal added relative to the La/NaZSM-5 catalyst was proposed in a scheme including benzyl alcohol activated with the added alkali metal and gaseous oxygen.

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