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Role of potassium added to Ce/NaZSM-5 catalyst in partial oxidation activity of benzyl alcohol

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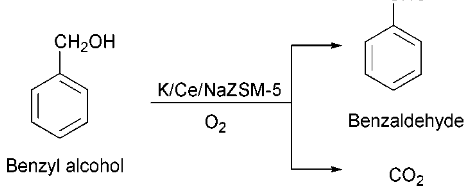
The vapor-phase catalytic oxidation of benzyl alcohol was carried out over cerium-impregnated NaZSM-5 (Ce/NaZSM-5) and K-added Ce/NaZSM-5 catalysts. The main products were benzaldehyde and carbon dioxide, together with trace amounts of benzene and toluene. The effect of the added K on the catalytic activity in the benzyl alcohol oxidation was different by the amount of supported Ce (Ce: 1.4×10^{-2}–7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$, low Ce (Ce_L): $\simeq 10^{-2}$ mmol g(NaZSM-5)$^{-1}$, high Ce (Ce_H): $\simeq 10^{-1}$ mmol g(NaZSM-5)$^{-1}$). The BET surface area and the temperature-programmed oxidation (TPO) of the fresh and the used K-added Ce/NaZSM-5 catalysts was measured to obtain information on the role of the added K in the catalytic activity of the benzyl alcohol oxidation. The amount of O_2 uptake of the pre-reduced K-added Ce_H/NaZSM-5 catalysts was also measured to estimate the ability to store the oxygen species on the cerium. The main role of potassium added to the high Ce-loaded NaZSM-5 (Ce_H/NaZSM-5) catalyst was to prevent the build-up of coke-like materials on the catalyst surface during the oxidation and so prolong the catalytic life.

Cerium oxides have been utilized as one of the components in the three-way automobile catalyst, in which cerium oxide catalysts have been reported to function as a oxygen reservoir and/or a heat-proof component. The addition of Ce to Cu-NaZSM-5, which has been reported[1] to be specifically active for NO_x decomposition, caused an increase in the NO_x decomposition activity.[2] Cerium-supported ZSM-5 catalyst promoted by alkaline earth metals has been shown to be effective for the SCR of NO using propene as a reductant.[3,4] The addition of Ce to the Ag-ZSM-5 catalyst promoted the oxidation of NO to NO_2.[5]

The liquid-phase oxidation of alcohol derivatives to the corresponding aldehydes using an oxidant is one of the environmentally loaded reactions. From the green chemistry point of view, gas-phase catalytic oxidation will be preferable because of an easy separation of product from catalyst, no use of solvent, and no generation of the used oxidant. The development of a catalyst with high selectivity for the partial oxidation is necessary in the gas-phase catalytic reaction. We have reported the effect of the alkali metal added to Cu-supported ZSM-5 catalysts on the gas-phase catalytic oxidation of benzyl alcohol, in which the added alkali metals have been reported to effectively promote the partial oxidation activity.[6–10] The addition of alkali metals to cerium-supported ZSM-5 catalyst causes an increase in the activity of the partial oxidation of benzyl alcohol when the amounts of the supported cerium are lower but inversely causes a decline in the oxidation activity using the cerium-supported ZSM-5 catalyst with a higher cerium content.[11]



In this study, the effect of the alkali metal (K) added to the cerium-supported NaZSM-5 (Ce/NaZSM-5) catalyst on the catalytic activity in benzyl alcohol oxidation was investigated using the Ce/NaZSM-5 catalysts with a wide variety of cerium contents. The added K was found to have different functions in the catalysts with lower and higher contents of cerium. The role of potassium added to the Ce/NaZSM-5 with a lower content of cerium has been discussed previously.[11] The role of the potassium added to the Ce/NaZSM-5 catalyst with a higher content of cerium will be mainly discussed in this paper.

Experimental

Catalysts

NaZSM-5 zeolite was synthesized according to a patent.[12] The synthesized ZSM-5 zeolite was twice treated with 1 M $NaNO_3$ at 343–358 K for 1 h to obtain NaZSM-5 zeolite ion-exchanged with 100% Na cation. The NaZSM-5 zeolite was dried at 383 K overnight and calcined at 773 K for 5 h under flowing air. The Si/Al atomic ratio determined by an atomic absorption spectrometer (Shimazu Type AA-630-01) was 58. HZSM-5 zeolite was prepared by ion-exchanging with 1 M NH_4NO_3 three times, drying overnight, and calcining at 773 K for 5 h. Cerium-supported NaZSM-5 (Ce/NaZSM-5) was prepared using $Ce(CH_3COO)_3 \cdot H_2O$ as a cerium source by impregnation followed by calcination at 773 K for 5 h. Alkali metal (K)-supported Ce/NaZSM-5 (K/Ce/NaZSM-5) was prepared by impregnating CH_3COOK, drying at 393 K overnight, and calcining at 773 K for 3 h in a flow of air. MCM-41 was synthesized by a sol–gel method at room temperature as described previously.[13] The BET surface area was 950 m^2 g^{-1}. CeO_2 was prepared by calcining $Ce_2(CH_3COO)_3$ at 773 K for 5 h in flowing air. K-added CeO_2 (K/CeO_2) was prepared by impregnating aqueous CH_3COOK, drying overnight, and calcining at 773 K for 3 h in a flow of air.

Gas-phase catalytic oxidation of benzyl alcohol

The gas-phase catalytic oxidation of benzyl alcohol was carried out using a continuous fixed-bed Pyrex microreactor (id 15 mm) under atmospheric pressure. The catalyst (0.15 g) placed in the reactor was pretreated at 773 K for 2 h in flowing air. The reaction was started by feeding benzyl alcohol from a microfeeder. Typical reaction conditions were as follows: $W/F = 6.52$ g(cat) min mol^{-1}; W (catalyst weight) = 0.15 g; F (total molar flow) = 0.023 mol min^{-1}; $N_2 : O_2$: benzyl alcohol = 32 : 3 : 1 (mol ratio). The products were analyzed by gas chromatography; details of these analyses have been described elsewhere.[11] The conversion, the yield, and the selectivity were defined[7] as follows:

Conversion of benzyl alcohol (%)

$$= \frac{[\text{Balde}] + \frac{1}{7}[\text{CO}_2] + [\text{Benz}] + [\text{Tolu}]}{[\text{Balco}]} \times 100$$

$$\text{Yield of benzaldehyde (\%)} = \frac{[\text{Balde}]}{[\text{Balco}]} \times 100$$

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

Selectivity of benzaldehyde (%)

$$= \frac{[\text{Balde}]}{[\text{Balde}] + \frac{1}{7}[\text{CO}_2] + [\text{Benz}] + [\text{Tolu}]} \times 100$$

Selectivity of CO_2 (%)

$$= \frac{\frac{1}{7}[\text{CO}_2]}{[\text{Balde}] + \frac{1}{7}[\text{CO}_2] + [\text{Benz}] + [\text{Tolu}]} \times 100$$

Where [ ] is the number of moles produced or fed, Balco = benzyl alcohol, Balde = benzaldehyde, Benz = benzene, Tolu = toluene and CO_2 = carbon dioxide. The carbon balances obtained were usually more than 90%.

Measurement of BET surface area of catalysts

The BET surface area of the catalysts was measured using a gas-adsorption apparatus equipped with a digital manometer.

Measurement of the amount of O_2 uptake of the pre-reduced catalysts

The amount of O_2 uptake of a catalyst (0.05 g) pre-reduced by CO (20 kPa, 773 K, 1 h) was measured using semimicro-gas-absorption equipment with a capillary-glass sample tube. Details of the experimental procedure have been described previously.[10,11]

Diffuse reflectance (DR) spectra of catalysts

The DR spectra of the catalysts with high cerium loading were observed at room temperature using an electronic absorption spectrophotometer (Hitachi type U-3210D) equipped with an integral sphere (Hitachi 150-0902). The catalyst samples were placed in an *in situ* cell and were pretreated using a vacuum line. The observed spectra were converted into the corresponding Kubelka–Munk (KM) function using an applied program.

Temperature-programmed oxidation (TPO) of used catalysts

The TPO of the catalysts (10 mg) used in the benzyl alcohol oxidation was performed under flowing $N_2/O_2(=4:1)$ in the temperature range of room temperature to 773 K at a programmed 20 K min^{-1} using a thermal balance attached to a differential thermal analysis (DTA) unit (Shimazu type DTG-40). NaZSM-5 zeolite was used as a reference for the DTA.

Results and discussion

Catalytic activity of Ce/NaZSM-5 catalysts and K-added counterparts in benzyl alcohol oxidation

The main products obtained in the gas-phase catalytic oxidation of benzyl alcohol over Ce/NaZSM-5 catalyst and K-added counterparts were benzaldehyde and CO_2. Fig. 1 illustrates the influence of the added K/Ce atomic ratio on the yields of both benzaldehyde and CO_2 using a low Ce (Ce: $\simeq 10^{-2}$ mmol g(NaZSM-5)$^{-1}$) supported NaZSM-5 (Ce_L/NaZSM-5) and the K-added counterpart (K/Ce_L/NaZSM-5) catalysts. The yield of benzaldehyde had a maximum value at the added K/Ce ratio of around 4, but the CO_2 yield did not vary by adding K to the Ce/NaZSM-5. Thus the addition of K to the Ce_L/NaZSM-5 (Ce, 7.1×10^{-2} mmol g(NaZSM-5)$^{-1}$) caused both a higher yield and selectivity for benzaldehyde. The apparent activation energy of benzaldehyde formation catalyzed by K(4)/Ce_L/NaZSM-5 (added K/Ce atomic ratio, 4; Ce, 7.1×10^{-2} mmol g(NaZSM-5)$^{-1}$), which was calculated using the data at 653 and 673 K, was 170.9 kJ mol^{-1}.

The dependence of the yield of both benzaldehyde and CO_2 on the Ce loading was investigated using both Ce/NaZSM-5 and K(4)/Ce/NaZSM-5 (added K/Ce atomic ratio, 4) catalysts (Fig. 2(A)). The yield of benzaldehyde catalyzed by Ce/NaZSM-5 increased monotonically with the increase in the Ce loading. The K(4)/Ce/NaZSM-5 catalyst gave a maximum value in the yield of benzaldehyde at a Ce loading of around 0.2 mmol g(NaZSM-5)$^{-1}$. Thus the added K caused a decrease in the oxidation activity of the Ce_H/NaZSM-5 catalysts with the higher Ce loading. The yields of CO_2 by the K(4)/Ce/NaZSM-5 catalyst were lower than those by the Ce/NaZSM-5 catalyst regardless of the Ce loading. Fig. 2(B) illustrates the dependence of the turnover frequencies (TOFs (h^{-1}); benzaldehyde formed per unit time per Ce) of both Ce/NaZSM-5 and the K(4)/Ce/NaZSM-5 catalysts based on the experimental results of Fig. 2(A). The TOF was defined conveniently using the total amount of impregnated Ce, in place of the amount of surface Ce. The TOF of the Ce/NaZSM-5 did not vary greatly with the increase in the Ce loading. The TOF of the K(4)/Ce/NaZSM-5 catalyst had a maximum value at a Ce loading of around 0.2 mmol g(NaZSM-5)$^{-1}$, and a higher Ce loading caused a considerable reduction in the TOF.

Fig. 3(A) shows the dependence of the time course of the yield of benzaldehyde on the added K/Ce ratio of K/Ce_H/NaZSM-5 (Ce: 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalyst. The yield of benzaldehyde catalyzed by the

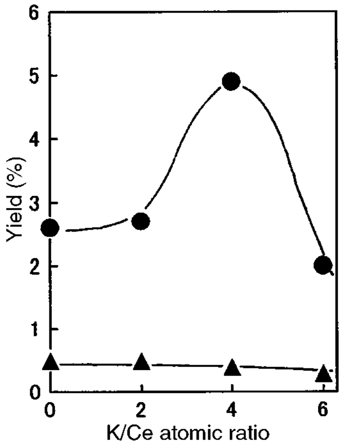


Fig. 1 Dependence of benzaldehyde and CO_2 yields on the added K/Ce atomic ratio using a low-Ce-supported NaZSM-5 catalyst (Ce_L/NaZSM-5). Catalyst, K/Ce_L/NaZSM-5 (Ce = 7.1×10^{-2} mmol g(NaZSM-5)$^{-1}$); reaction temperature, 653 K; ●, yield of benzaldehyde; ▲, yield of CO_2.

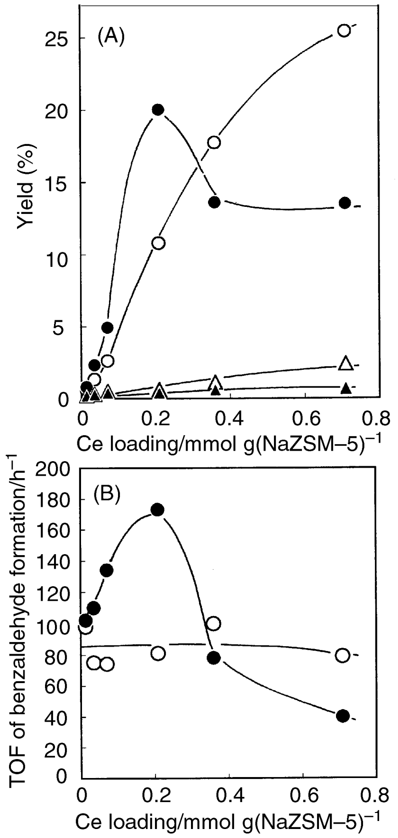


Fig. 2 Dependence of benzaldehyde and CO_2 yields (A) and turnover frequency (TOF) (B) on Ce loading. Reaction temperature, 653 K. (A) ●, ▲, K(4)/Ce/NaZSM-5 catalyst (K/Ce atomic ratio = 4); ○, △ Ce/NaZSM-5 catalyst; ●, ○, yield of benzaldehyde; ▲, △, yield of CO_2. (B) ●, K(4)/Ce/NaZSM-5 catalyst (K/Ce atomic ratio = 4); ○, Ce/NaZSM-5 catalyst.

Ce_H/NaZSM-5 without added K decreased with time on stream although the initial yield was high. The addition of K to the Ce/NaZSM-5 catalyst inhibited the deactivation of the oxidation activity. The yield of benzaldehyde at steady state (time on stream of 2–4 h) catalyzed by the K(2)/Ce_H/NaZSM-5 was thus higher than that catalyzed by the Ce_H/NaZSM-5 without added K. Too high a loading of K (K/Ce = 8) caused a sharp decrease in the yield of benzaldehyde. The influence of added K on the yield of benzaldehyde by the K/Ce_H/NaZSM-5 (Ce: 7.1×10^{-1} mmol g(NAZSM-5)$^{-1}$) catalyst is illustrated in Fig. 3(B). The yield of benzaldehyde catalyzed by the Ce_H/NaZSM-5 without the added K decreased with the time on stream. The addition of K (K/Ce = 0.4) caused no improvement in the deactivation, but only a decrease in the oxidation activity. The higher addition of K (K/Ce = 4) did not cause deactivation although the yield of benzaldehyde decreased. The BET surface areas of both the Ce_H/NaZSM-5 (Ce: 7.1×10^{-1} mmol g(NAZSM-5)$^{-1}$) and the K-added (K/Ce = 4) counterpart were 240 and 40 m^2 g^{-1}, respectively. The sharp decrease in the BET surface area upon the addition of a large amount of K will be one of the reasons for the decline in the oxidation activity.

The dependence of the yields of both benzaldehyde and CO_2 on the time on stream was investigated for a prolonged time using both Ce_H/NaZSM-5 (7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$) and K(4)/Ce_H/NaZSM-5 (2.1×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalysts (Fig. 4). The yield of benzaldehyde produced by the former catalyst monotonically decreased with the time on stream. The K(4)/Ce_H/NaZSM-5 catalyst was not deactivated in the region of the time on stream measured. The yields of benzaldehyde obtained by both catalysts resulted in almost the same value at the time on stream of *ca.* 8 h. The yields of

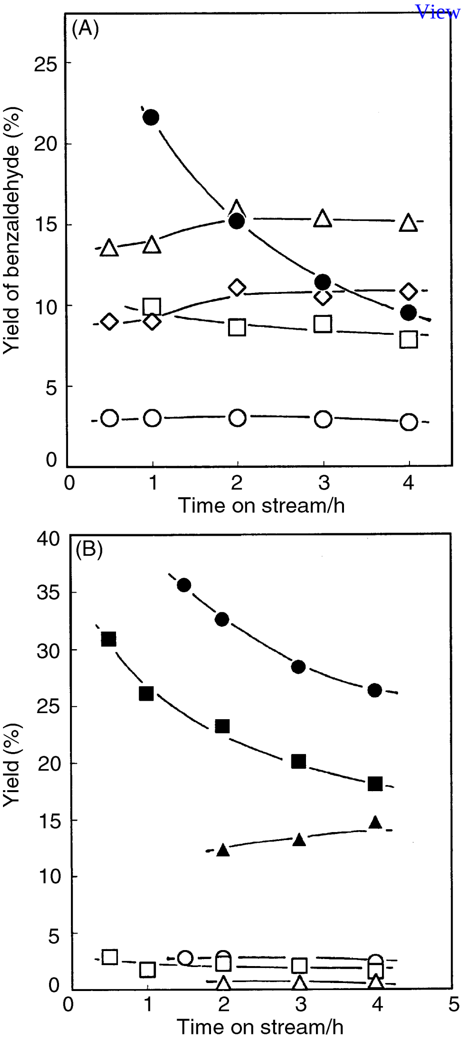


Fig. 3 Effect of added K/Ce on product yield using K/Ce_H/NaZSM-5 catalyst. Reaction temperature, 653 K. (A) Catalyst, K/Ce_H/NaZSM-5 (Ce = 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$); ●, K/C = 0; □, K/Ce = 1; △, K/Ce = 2; ◇, K/Ce = 4; ○, K/Ce = 8. (B) Catalyst, K/Ce_H/NaZSM-5 (Ce = 7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$); ●, K/Ce = 0; ■, K/Ce = 0.4; ▲, K/Ce = 4; ○, K/Ce = 0; □, K/Ce = 0.4; △, K/Ce = 4; ●, ■, ▲, yield of benzaldehyde; ○, □, △, yield of CO_2.

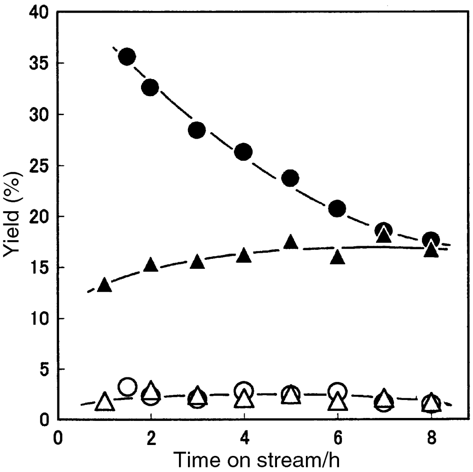


Fig. 4 Plot of product yields *vs.* time on stream using Ce_H/NaZSM-5 (Ce: 7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$) and K(4)/Ce_H/NaZSM-5 (Ce: 2.1×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalysts. Reaction temperature, 653 K; ●, ○, Ce_H/NaZSM-5 (Ce: 7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$); ▲, △ K(4)/Ce_H/NaZSM-5 (Ce: 2.1×10^{-1} mmol g(NaZSM-5)$^{-1}$); ●, ▲, yield of benzaldehyde; ○, △, yield of CO_2.

Table 1 Effect of support on the yield of benzaldehyde using low-Ce (Ce_L)-supported catalysts[a]

Catalyst	Conversion[b] (%)	Yield[b] (%)			
		Benzaldehyde	CO_2	Benzene	Toluene
NaZSM-5	1.7	1.3	0.3	Trace	0.1
K/NaZSM-5	2.4	1.8	0.4	0.1	0.1
Ce_L/NaZSM-5	6.5	5.3	1.1	Trace	0.1
K/Ce_L/NaZSM-5	13.7	12.4	1.1	0.1	0.1
HZSM-5	4.7	3.6	0.9	0.2	Trace
Ce_L/HZSM-5	4.7	3.6	0.9	Trace	0.2
K/Ce_L/HZSM-5	10.9	8.6	2.0	0.2	0.1
NaY	4.9	2.7	1.8	0.2	0.2
Ce_L/NaY	5.3	3.8	1.1	0.1	0.3
K/Ce_L/NaY	11.0	9.5	1.2	0.2	0.1
Al_2O_3	3.8	2.9	0.6	Trace	0.3
Ce_L/Al_2O_3	4.4	3.8	0.5	Trace	0.1
K/Ce_L/Al_2O_3	17.5	16.4	0.9	0.1	0.1
SiO_2	1.8	1.4	0.2	0.1	0.1
Ce_L/SiO_2	6.3	4.9	1.0	0.2	0.2
K/Ce_L/SiO_2	5.2	4.4	0.5	0.2	0.1
MCM-41	1.2	0.8	0.1	0.2	0.1
Ce_L/MCM-41	3.1	1.8	1.1	0.1	0.1
K/Ce_L/MCM-41	3.0	2.6	0.2	0.1	0.1

[a] Ce (Ce_L) loading, 7.14×10^{-2} mmol g(support)$^{-1}$ (1.0 wt.%); added K/Ce atomic ratio = 4; reaction temperature, 673 K. [b] Average value of three data obtained at the time-on-stream of 2, 3 and 4 h.

CO_2 over both catalysts were low and almost constant with the time on stream.

Too great an amount of Ce supported on the NaZSM-5 is supposed to cause the formation of CeO_2 on the surface of the NaZSM-5. CeO_2 has been utilized as a support for CO oxidation[14–16] and as a catalyst for the conversion reaction of low-weight hydrocarbons.[17] The catalytic activity for benzyl alcohol oxidation of CeO_2 itself was investigated using three physically mixed catalytic systems of CeO_2 + NaZSM-5, CeO_2 + K(4)/NaZSM-5 and K(4)/CeO_2 + NaZSM-5 (Fig. 5). The amounts of Ce in the three catalysts were the same, and the added K/Ce atomic ratios of the latter two systems were kept at 4. The yield of benzaldehyde catalyzed by the CeO_2 + NaZSM-5 system considerably decreased with time on stream. The deactivation was to some extent inhibited using the CeO_2 + K(4)/NaZSM-5 catalytic system. The CeO_2 + K(4)/NaZSM-5 catalyst used was confirmed to be almost as white as a fresh one, differing from the CeO_2 + NaZSM-5 catalytic system, in which the used one turned brown. The oxidation activity of the K(4)/CeO_2 + NaZSM-5 catalyst was rather low. The covering of the added K on the active CeO_2 sites may cause the low catalytic activity for benzyl alcohol oxidation.

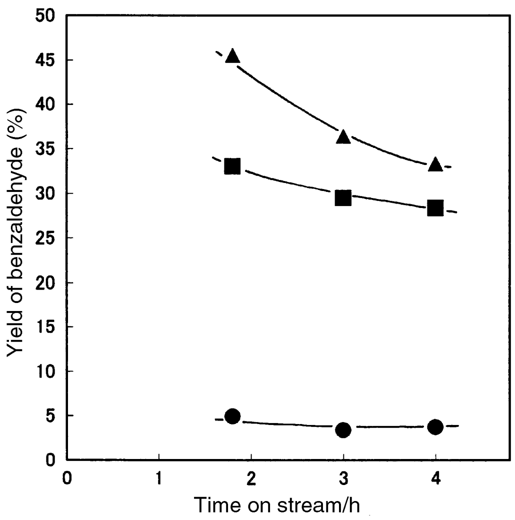


Fig. 5 Yield of benzaldehyde obtained using CeO_2 + NaZSM-5, CeO_2 + K(4)/NaZSM-5 and K(4)/CeO_2 + NaZSM-5 catalytic systems. Reaction temperature, 623 K; amount of Ce, 9.7×10^{-2} mmol; amount of K, 3.9×10^{-1} mmol (K/Ce = 4); ▲, CeO_2 + NaZSM-5; ■, CeO_2 + K(4)/NaZSM-5; ●, K(4)/CeO_2 + NaZSM-5.

Benzyl alcohol oxidation catalyzed by Ce-supported oxides with and without added K

Benzyl alcohol oxidation was attempted using low-Ce-supported catalysts (Ce_L/support) on various oxides with and without added K (Table 1). The supports without Ce and K were also utilized as catalysts. The effect of added K on the yield of benzaldehyde varied considerably depending on the oxide support. The yield of benzaldehyde by Ce_L catalysts supported on NaZSM-5, HZSM-5, NaY and Al_2O_3 was promoted with the addition of K. The Ce_L catalyst supported on SiO_2 and MCM-41 showed no promotion effect for benzaldehyde formation on adding K, but the addition of K to the Ce_L/MCM-41 catalyst caused inhibition of the deactivation of both benzaldehyde formation and CO_2 formation (Fig. 6). The results in Table 1 and Fig. 6 were obtained under the condition of an added K/Ce atomic ratio of 4. However, the depen-

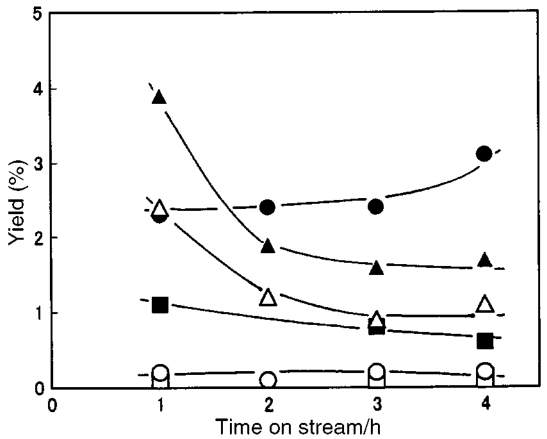


Fig. 6 Product yields obtained using MCM-41, Ce_L/MCM-41 and K/Ce_L/MCM-41 catalysts. Reaction temperature, 673 K; amount of Ce, 7.1×10^{-2} mmol g(support)$^{-1}$; amount of K, 2.9×10^{-1} mmol g(support)$^{-1}$; ■, □, MCM-41; ▲, △, Ce_L/MCM-41; ●, ○, K/Ce_L/MCM-41; ■, ▲, ●, yield of benzaldehyde; □, △, ○, yield of CO_2.

dence of benzyl alcohol oxidation on the added K/Ce may be different with the supports utilized. The optimum value of the added K/Ce for the benzaldehyde formation may thus vary with the support.

O_2 uptake of both the Ce_H/NaZSM-5 catalyst and the K-added counterpart which were prereduced

The influence of the added K on the amount of O_2 uptake of the prereduced catalysts was investigated using the Ce_H/NaZSM-5 (Ce, 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalysts (Fig. 7). The amount of O_2 uptake was almost constant with the variation in the added K/Ce atomic ratios of 0 to 8, the behavior of which is quite different from the variation in the yield of benzaldehyde. A similar dependence between the benzaldehyde yield and the amount of O_2 uptake on the added Rb/Ce atomic ratio, with both maximum values observed at an atomic ratio of around 4, has been observed[11] using low-Ce-supported NaZSM-5 (Ce_L/NaZSM-5) catalysts (Ce, $\simeq 10^{-2}$ mmol g(NaZSM-5)$^{-1}$) which were prereduced under CO and degassed. Based on the results of both the O_2 uptake and the reaction behavior in the absence of gaseous O_2, one role of an added alkali metal such as Rb was suggested to be in increasing the amount of the sorbed O_2 species, which had a strong correlation with the formation of benzaldehyde.[11] On the contrary, the high-Ce-supported NaZSM-5 (Ce_H/NaZSM-5) catalyst (Ce, 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$) utilized in this study showed no similar dependence between the amount of O_2 uptake and the benzaldehyde yield on the added K/Ce ratio, as indicated in Fig. 7. The large Ce particle corresponding to the Ce_H species may not be greatly influenced by the added alkali metal because the surface area of the Ce_H species will be considerably lower and the contact between the added alkali metal and the Ce_H species will be small. On the other hand, the degree of dispersion of the Ce_L species will be comparatively higher, and the high surface area may contribute to the variation of the redox properties (O_2 uptake) of the Ce_L species seen upon adding alkali metal.

BET surface area of K-added Ce_H/NaZSM-5 catalysts

The dependence of the surface area of the K/Ce_H/NaZSM-5 catalysts (Ce, 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$) on the added K/Ce atomic ratio was investigated using a BET method. The BET surface area of the K/Ce_H/NaZSM-5 catalyst, together with the yield of benzaldehyde, decreased with added K/Ce atomic ratios of more than 2 (Fig. 8). The results obtained here indicates that too much added K will deposit outside of the zeolite and narrow the mouth of the zeolite pores and/or block completely the opening of the mouth. One important reason for the benzaldehyde yield declining with the increase in the added K/Ce ratio will be the blockage of the pore of the zeolite support.

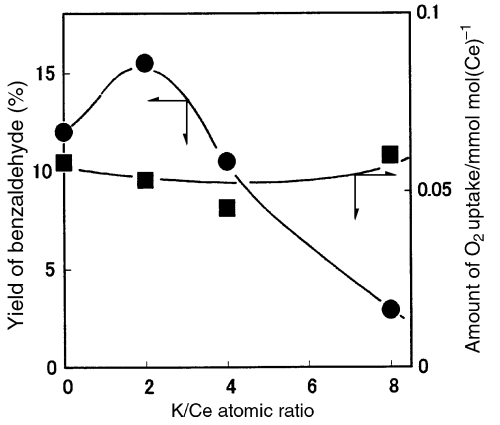


Fig. 7 Influence of added K/Ce_H atomic ratio on yield of benzaldehyde (●) and O_2 uptake (■). Catalyst, K/Ce_H/NaZSM-5 (Ce: 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$); reaction temperature, 653 K; temperature for O_2 uptake, 653 K.

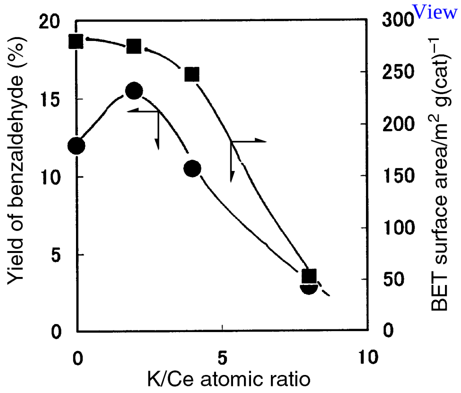


Fig. 8 Influence of added K/Ce_H atomic ratio on the yield of benzaldehyde (●) and BET surface area (■). Catalyst, K/Ce_H/NaZSM-5 (Ce: 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$); reaction temperature, 653 K.

Deposition of carbonaceous material on the Ce/NaZSM-5 used and the K-added counterpart

It was visually observed that the Ce_H/NaZSM-5 (Ce, 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalyst during the benzyl alcohol oxidation turned from white to dark brown. The used K(4)/Ce_H/NaZSM-5 (Ce, 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalyst was light brown, but the K(8)/Ce_H/NaZSM-5 (Ce, 2.9×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalyst remained white. Based on these visual observations, the added K will be related to the amount of the carbonaceous material accumulated on the catalysts during the benzyl alcohol oxidation. Benzyl alcohol and benzaldehyde are thought to be precursors for carbonaceous materials which will be formed through cyclization, dehydrogenation, further alkylation, *etc*., leading to polyaromatics.[18,19] The sites on which coke formation is promoted will be Na^+ and/or H^+ sites ion-exchanged with H_2O formed during the oxidation. The TPO of the Ce_H/NaZSM-5 used and the K added counterparts was carried out using a thermal balance attached to the DTA equipment (Fig. 9). The DTA curve of the Ce_H/NaZSM-5 catalyst showed a considerably large exothermic peak starting from around 573 K, accompanied by a large decrease in the weight of the catalyst used (Fig. 9(A)). TPO of the K(4)/Ce_H/NaZSM-5 catalyst (Fig. 9(B)) also showed an exothermic peak, with a peak area rather smaller than that of the Ce_H/NaZSM-5 catalyst used. (The area of the exothermic area generated by the K(4)/Ce_H/NaZSM-5 catalyst used was *ca.* one-third of that by the used Ce_H/NaZSM-5 catalyst.) The smaller weight loss of the K(4)/Ce_H/NaZSM-5 catalyst used was accompanied by a smaller exothermic peak. The exothermic peak generated by the TPO of the K(8)/Ce_H/NaZSM-5 catalyst was very small, and the corresponding weight loss was hardly observed (Fig. 9(C)). The results obtained in Fig. 9 indicate that the K added to the Ce_H/NaZSM-5 catalyst inhibits the accumulation of carbon-like materials on the catalyst. Thus the main role of the K added to the high-Ce-supported NaZSM-5 is thought to be in impeding the deposition of carbonaceous materials that will cause deactivation of the catalyst. Coke formation on a non-acidic silica has been shown to be less than that on an acidic silica-alumina.[20] Coke deposition has been reported to become less serious as the strong acid sites of silica-alumina were weakened by NaOH treatment.[21] The difference in the dependence of the yield of benzaldehyde on the time-on-stream catalyzed by the Ce_H/NaZSM-5 and the K-added counterparts (Figs. 3 and 4) is ascribed to the role of the K added to the high-Ce-supported NaZSM-5 catalyst mentioned here.

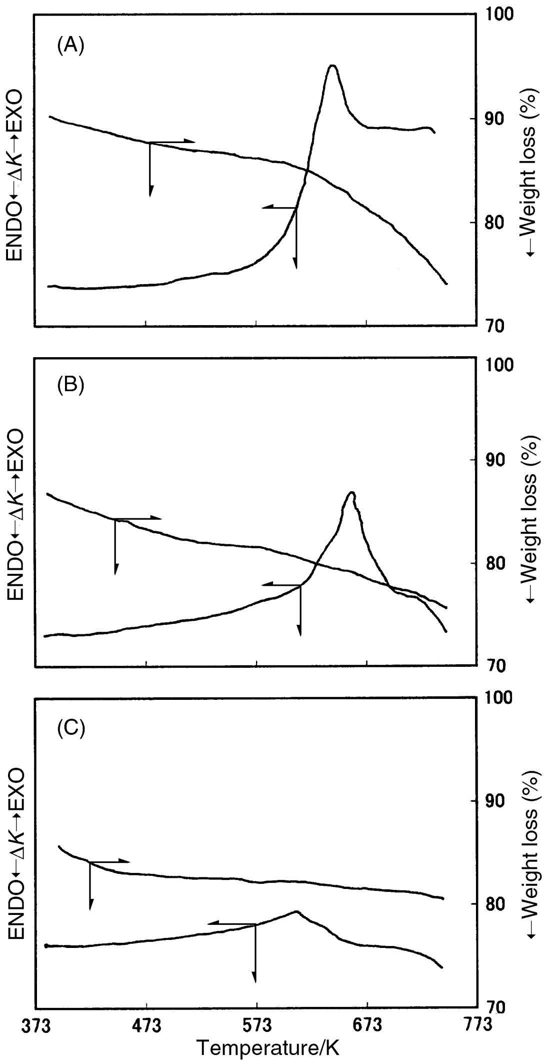


Fig. 9 Temperature-programmed oxidation (TPO) of Ce_H/NaZSM-5 and the K-added counterparts used. Sample, K/Ce_H/NaZSM-5 (Ce: 2.8×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalyst used for benzyl alcohol oxidation at 653 K for 4 h; (A) added K/Ce = 0; (B) added K/Ce = 4; (C) added K/Ce = 8.

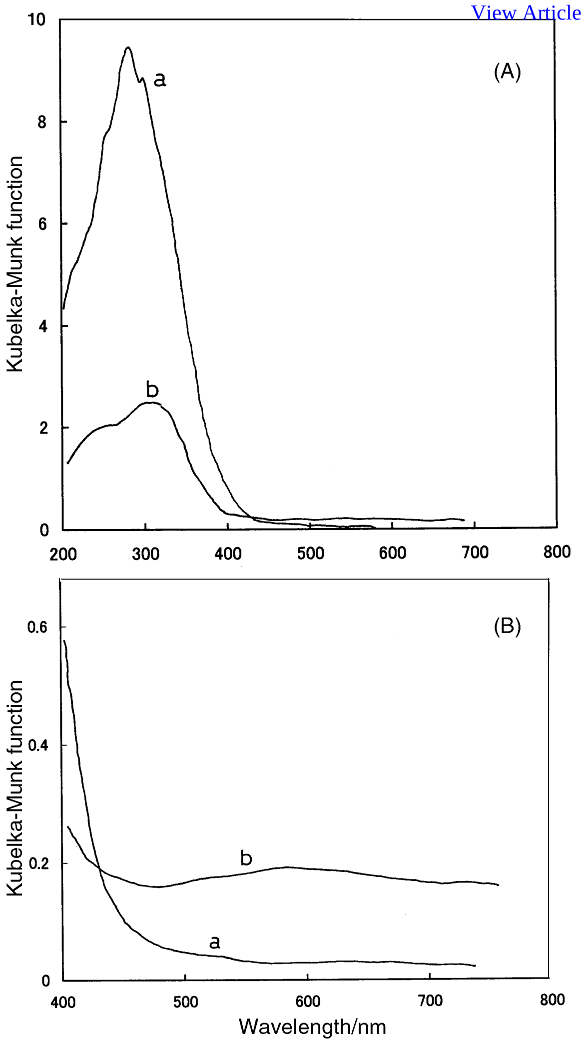


Fig. 10 Diffuse-reflectance (DR) spectra of Ce_H/NaZSM-5 (7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$). (A) a, Treated at 773 K for 1 h under O_2 followed by degassing at room temperature for 1 h; b, sample a was degassed at 773 K for 1 h and treated at 773 K for 1 h under CO followed by degassing at room temperature for 1 h. (B) Enlarged KM function of (A) in the wavelength region of 400–800 nm.

We have previously reported[11] that the alkali metal added to a low-Ce-supported NaZSM-5 catalyst (Ce_L/NaZSM-5, Ce, $\simeq 10^{-2}$ mmol g(NaZSM-5)$^{-1}$) acts as a promoter for the benzyl alcohol oxidation, particularly for the activity of the partial oxidation. The added alkali metal has been suggested[11] to play an important role in increasing the O_2 uptake, of which the sorbed O_2 species will participate in the partial oxidation of benzyl alcohol. However, the K added to a high-Ce-supported NaZSM-5 catalyst (Ce_H/NaZSM-5; Ce, more than around $\simeq 10^{-1}$ mmol g(NaZSM-5)$^{-1}$) caused instead a decline in the yield of benzaldehyde and did not act as a promoter, although the deactivation with the time on stream was inhibited as described previously. Thus the added K was confirmed to have a different role in the Ce_L/NaZSM-5 and in the Ce_H/NaZSM-5 catalysts. The reversal of the TOF of the Ce/NaZSM-5 and the K(4)/Ce/NaZSM-5 catalysts at a Ce loading of more than around 3.5×10^{-1} mmol g(NaZSM-5)$^{-1}$ (Fig. 2(B)) indicates the conversion of the role of the added K depending on the Ce loading.

Diffuse reflectance (DR) spectra of the Ce_H/NaZSM-5 and the K added-counterpart

The DR spectra of the Ce_H/NaZSM-5 (Ce, 7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$) and the K-added counterparts (K/Ce_H/NaZSM-5; Ce, 7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$); added K/Ce atomic ratio, 0.4, 4) were measured to investigate the influence of the added K on the redox behavior of the catalysts. The DR spectra of the Ce_H/NaZSM-5 catalysts treated with O_2 and with CO at 773 K for 1 h are illustrated in Fig.

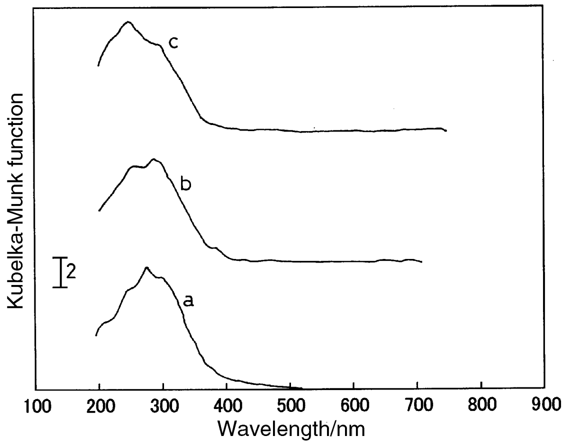


Fig. 11 DR spectra of preoxidized K/Ce_H/NaZSM-5 (Ce: 7.1×10^{-1} mmol g(NaZSM-5)$^{-1}$) catalysts. Degassed at 773 K for 0.5 h and treated at 773 K for 1 h under O_2 followed by degassing at room temperature for 1 h; a, added K/Ce_H = 0; b, added K/Ce_H = 0.4; c, added K/Ce_H = 4.

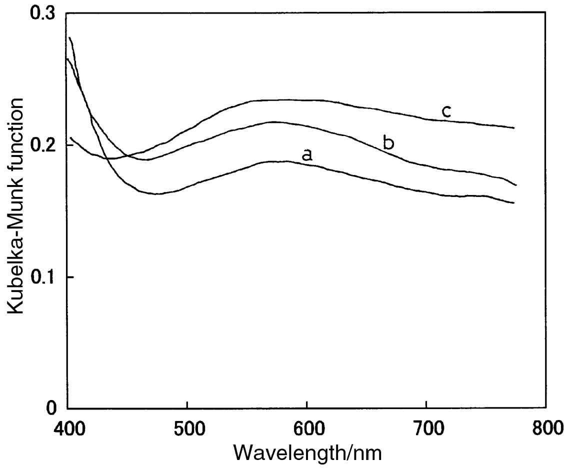


Fig. 12 DR spectra of prereduced K/Ce_H/NaZSM-5 (Ce: 7.1 × 10^{-1} mmol g(NaZSM-5)$^{-1}$) catalysts. The sample of Fig. 11 was degassed at 773 K for 1 h and treated at 773 K for 1 h under CO followed by degassing at room temperature for 1 h; a, added K/Ce_H = 0; b, added K/Ce_H = 0.4; c, added K/Ce_H = 4.

10. Two peaks at 280 and 295 nm and two shoulders at 210 and 260 nm were observed in the oxidized Ce_H/NaZSM-5 catalysts treated with O_2 (Fig. 10(A), (a)). Viana *et al.*[22] and Bensalem *et al.*[23,24] have identified both the peaks at 280 and 294 nm as charge transfer bands between Ce^{4+} and oxygen and the peaks at 210 and 260–265 nm as based on a Ce^{3+} transition and the charge transfer between Ce^{3+} and oxygen. The Ce^{4+} species will be mainly present in the oxidized Ce_H/NaZSM-5 catalyst, together with small amounts of the Ce^{3+} species. The DR peaks at 200–400 nm of the reduced Ce_H/NaZSM-5 catalyst are considerably decreased in intensity (Fig. 10(A), (b)), and, inversely, the intensity of the KM function at more than 450 nm increased by treatment with CO (Fig. 10(B), (b)). A peak at 588 nm has been reported to increase with the increase in the temperature of treating CeO_2 with H_2 and is attributed to the reduction of CeO_2 to Ce_2O_3.[25] Thus the Ce_H/NaZSM-5 catalyst showed a redox behavior in oxidizing and reducing atmospheres. The DR spectra of the K/Ce_H/NaZSM-5 catalysts (added K/Ce, 0.4, 4) treated with O_2 at 773 K are illustrated, together with the oxidized Ce_H/NaZSM-5 without added K, in Fig. 11. The intensities and the shape of the three DR peaks were substantially similar, although the peak at around 295 nm tended to decrease and the peak at around 250 nm tended to increase in the case of the K(4)/Ce/NaZSM-5 catalyst. The CO reduced forms of the three catalysts decreased in their intensities but the shape of the DR peaks at 200–400 nm were once again almost similar, though the peak at around 580–590 nm tended to increase by adding K to the Ce_H/NaZSM-5 catalyst (Fig. 12). Based on the DR spectra of the Ce_H/NaZSM-5 and the K-added counterparts, the addition of K to the Ce_H/NaZSM-5 catalyst has only a small influence on the redox properties. Thus the fraction of Ce^{+3} species in the K(4)/Ce_H/NaZSM-5 catalyst tended to be larger than that of the K-free counterpart in both oxidized and reduced types. This may be due to a partial charge transfer from the added K (as K_2O) to the Ce species. The decline in the partial oxidation activity by adding K to the Ce_H/NaZSM-5 catalyst can be partly interpreted by the decrease in the oxidized form of Ce, the Ce^{4+} species.

Conclusions

The influence of potassium (K) as an alkali metal added to the high-Ce-supported NaZSM-5 (Ce_H/NaZSM-5, Ce; $\simeq 10^{-1}$ mmol g(NaZSM-5)$^{-1}$) catalyst on the partial oxidation activity in the gas-phase catalytic oxidation of benzyl alcohol was found to be quite different from that of alkali metal added to the low-Ce-supported NaZSM-5 (Ce_L/NaZSM-5, Ce; $\simeq 10^{-2}$ mmol g(NaZSM-5)$^{-1}$): the K added to the Ce_H/NaZSM-5 catalyst caused a decrease in the catalytic activity of benzyl alcohol oxidation, although the deactivation of the K/Ce/NaZSM-5 catalyst with time on stream was inhibited. On the other hand, the alkali metal added to the Ce_L/NaZSM-5 catalyst promoted the catalytic activity, particularly the partial oxidation activity, in accordance with our previous study. The decrease in the amount of carbonaceous materials deposited on the catalyst by adding K to the Ce_H/NaZSM-5 catalyst was clearly observed using a thermal balance attached to DTA equipment. The decrease in the yield of benzaldehyde using the K/Ce_H/NaZSM-5 catalysts with K/Ce atomic ratios of more than *ca.* 2 was related to the decrease in the BET surface of the K/Ce_H/NaZSM-5 catalyst. The amount of O_2 uptake was hardly varied by adding K to the reduced Ce_H/NaZSM-5 catalyst, in agreement with the observation that the DR spectra of Ce_H/NaZSM-5 and the K-added counterpart in both the oxidized and the reduced forms were similar in both intensity and shape.

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