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Promoted partial oxidation activity of supported Ag catalysts in the gas-phase catalytic oxidation of benzyl alcohol

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Abstract

The gas-phase catalytic oxidation of benzyl alcohol was carried out using Ag catalysts impregnated on a SiO_2 or CaO support, as well as a potassium-added counterpart ($K/Ag/SiO_2$), to clarify the surface state of the Ag species active in the oxidation reaction, the effect of the basic support and the added alkali metal. Benzaldehyde was obtained as the main oxidation product. The effects of the calcination temperature of the Ag/SiO_2 catalyst and the reaction temperature on oxidation activity were investigated. The benzaldehyde yield markedly increased between 553 and 593 K. Increasing the calcination temperature from 773 to 1173 K also caused a significant increase in partial oxidation activity. Both a CaO support for the Ag species and potassium added to the Ag/SiO_2 catalyst promoted partial oxidation at a comparatively low reaction temperature. X-ray diffraction and extended X-ray absorption fine structure demonstrated that a high calcination temperature, a basic support, and addition of an alkali metal led to a more ready reduction of the supported Ag to metallic Ag. Oxidized surface Ag species on the metallic Ag were inferred to be the active Ag components for the partial oxidation of benzyl alcohol based on the amount of O_2 uptake and the diffuse reflectance spectra of the supported Ag catalysts.

Keywords: Oxidation; Supported Ag catalysts; Alkali metal; Alkaline earth metal; Benzyl alcohol; Benzaldehyde; Diffuse reflectance spectra; Extended X-ray absorption fine structure

1. Introduction

Supported Ag catalysts have been reported to be highly effective for the practical oxidation processes of formaldehyde from methanol [1] and ethylene oxide from ethylene [2–9]. In particular, the production of ethylene oxide is exclusively carried out on Ag catalyst, promoted by alkali metals and supported on a nonporous form of α-alumina. Electrophilic adsorbed atomic oxygen species generated on the Ag catalysts have been suggested to attack the C=C bond in ethylene, whereas the more nucleophilic oxygen tends to activate C–H bonds [5,9]. Recently, Barteau et al. demonstrated by temperature-programmed desorption, high-resolution electron loss spectroscopy, and density functional theory [10–12] that surface oxametallacycles are important intermediates in Ag-catalyzed ethylene epoxidation. The structures of the transition states leading from the oxametallacycle were suggested to be crucial for ethylene oxide formation and for unselective combustion.

Alkali metals added to the supported Cu [13–19], Co [20,21], and Ce [22,23] catalysts promoted catalytic activity in the benzyl alcohol oxidation, particularly the partial oxidation. The added alkali metals increased the oxygen affinities of the Cu, Co, and Ce, catalysts and the adsorbed oxygen species seem to be effective for the partial oxidation of benzyl alcohol.

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In this study, the partial oxidation activities of Ag catalysts supported on SiO_2 or CaO, as well as the potassium-added SiO_2 counterpart, were investigated using the gas phase catalytic oxidation of benzyl alcohol. The effects of the reaction temperature and the calcination temperature of the catalysts on the partial oxidation were studied, as well as the X-ray diffraction (XRD), diffuse reflectance (DR), and extended X-ray absorption fine structure (EXAFS) spectra of the catalysts, to determine the factors directly relating to the catalytic activity.

2. Experimental

2.1. Catalysts

An Ag/SiO_2 (SiO_2: JRC-SIO-8) catalyst was prepared using $AgNO_3$ (Nacalai Tesque) in ethanol by conventional impregnation. The resulting Ag/SiO_2 was dried at 393 K overnight and calcined at 773 K for 5 h in flowing air. An alkali metal-added Ag/SiO_2 catalyst was prepared by impregnating CH_3COOK (Nacalai Tesque) on the Ag/SiO_2, drying at 393 K overnight, and calcining at 773 K for 5 h in flowing air. Ag catalysts impregnated on other oxide supports (CaO, Katayama Chemical; MgO, Wako Chemical; NaY, Tosoh ($Si/Al = 2.5$); NaZSM-5 and MCM-41, prepared in our lab) were prepared in a similar way.

2.2. Gas-phase catalytic oxidation

Benzyl alcohol (Nacarai Tesque) was used without further purification after confirming that no impurity was detected by gas-liquid chromatography (GLC). Oxygen and nitrogen gases were dried through a silica gel column before being supplied to the reaction system. The gas phase oxidation was performed using a conventional continuous-flow fixed-bed reactor (Pyrex, 15 mm i.d.) in the vertical position. After 0.2 g of catalyst was loaded in the reactor and pretreated at 773 K for 2 h in flowing air, the oxidation was started by supplying benzyl alcohol through a microfeeder to the reactor. Standard reaction conditions were $W/F = 8.70\ \mathrm{g_{cat}\ min/mol}$ (W, catalyst weight $= 0.2$ g; F, total flow rate $= 0.023$ mol/min), and N_2:O_2:benzyl alcohol $= 32:3:1$. The liquid phase products and the unreacted benzyl alcohol were collected in a trap cooled by a refrigerant (223 K; diethylmalonate + liquid N_2), diluted with 1 cm^3 dimethylformamide (internal standard), and analyzed using a GLC unit (Shimazu GC-8A) equipped with a flame ionization detector using a 2-m glass column filled with 5% PEG HIT on Uniport HP (60/80 mesh). The gaseous components were introduced to a 1-cm^3 gas sampler and analyzed by an intermediate-cell method [24] using a GLC unit (Shimazu GC-8A) equipped with a thermal conductivity detector using 1-m stainless steel columns filled with silica gel and molecular sieve at 393 and 298 K, respectively, under an H_2 carrier. The conversion, yield, and selectivity were obtained according to equations defined previously [15]. The obtained carbon balances were usually $>90\%$.

2.3. XRD measurement of the Ag/SiO_2 catalyst and the K-added counterparts

The XRD patterns of the Ag/SiO_2 catalyst and the K/Ag/SiO_2 catalyst were measured at room temperature using a Rigaku Model RINT 2100 XRD unit with a Cu-K_α source.

2.4. Catalyst O_2 uptake

A 20-mg portion of the supported Ag catalyst was degassed for 30 min followed by calcining at 773 K for 1 h under 20 kPa O_2. After degassing for 30 min, the catalyst was treated at 773 K for 1 h under 20 kPa CO followed by degassing. The total amount of O_2 uptake was measured after 5.2 kPa O_2 was introduced and the system had attained equilibrium. After degassing at room temperature for 1 h and once again introducing 5.2 kPa O_2, the reversible amount of O_2 uptake was measured. The difference between the total and the reversible amounts of O_2 uptake was estimated as the irreversible amount of O_2 uptake.

2.5. Diffuse reflectance (DR) spectra

The ultraviolet–visible (UV–vis) DR spectra of the supported Ag catalysts were measured using an electronic absorption spectrometer (Hitachi U-3210D) equipped with a 90∅ integral sphere (Hitachi 150-0902). The obtained data were converted to the corresponding Kubelka–Munk function using the application program U-3210/U-3410. Before DR measurement, the supported Ag catalysts held in a side arm of the sample cell were degassed for 15 min and treated at 773 K for 1 h under 150 Torr O_2 followed by degassing for 15 min. Reduction of the supported Ag catalysts was attempted by treating them with CO.

2.6. Ag EXAFS

The Ag K-edge EXAFS spectra of the supported Ag samples were obtained at the beam line BL01B1 of the Spring-8 synchrotron radiation facility at the Japan Synchrotron Radiation Research Institute (JASRI). All samples were pressed into self-supported disks without any binder. No chemical pretreatments were done for the samples, and all measurements were conducted with exposure of the samples to air. The Ag K-edge absorption spectra were recorded in the transmission mode at room temperature under atmospheric pressure. The storage ring energy was 8.0 GeV, and the ring current was 60–100 mA. A Si(311) double-crystal monochromator was used. The photon energy was calibrated by the characteristic pre-edge peaks due to the $3d \rightarrow 4\pi^*$ transition in the absorption of a Cu foil (8984.0 eV).

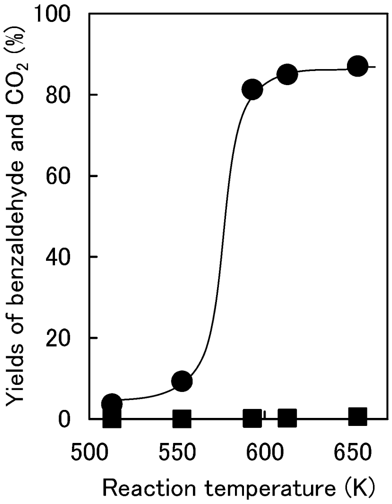


Fig. 1. Dependence of the yields of benzaldehyde and CO_2 on the reaction temperature. Catalyst, Ag(1.0)/SiO_2 calcined at 773 K; $W/F = 8.70$ g_{cat} min/mol, W (catalyst weight) = 0.2 g, F (total mole flow rate) = 0.023 mol/min; N_2:O_2:benzyl alcohol = 32:3:1; ●, benzaldehyde; ■, CO_2.

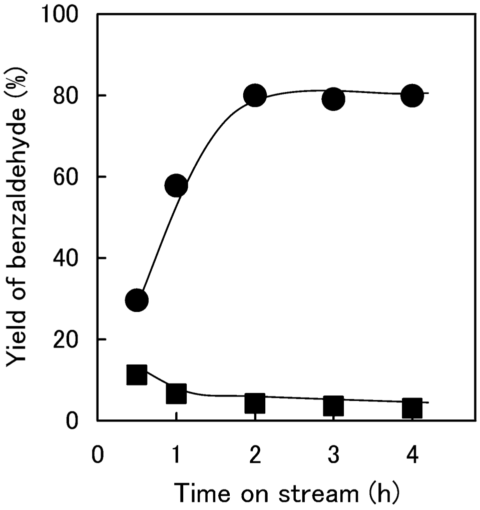


Fig. 2. Dependence of the yield of benzaldehyde on the time on stream. Catalyst, Ag(1.0)/SiO_2 calcined at 773 K; $W/F = 8.70$ g_{cat} min/mol, W (catalyst weight) = 0.2 g, F (total mole flow rate) = 0.023 mol/min; N_2:O_2:benzyl alcohol = 32:3:1; reaction temperature ●, 593 and ■, 513 K.

3. Results

No oxidation products were detected when the gas phase catalytic reaction of benzyl alcohol was attempted using only quartz sand diluent as a blank test. The main product of the gas phase oxidation of benzyl alcohol over the Ag/SiO_2 catalyst, and the K-added counterpart was benzaldehyde. Trace amounts of CO_2, benzene, and toluene were detected depending on the reaction conditions. Thus the selectivity for benzaldehyde produced over the supported Ag catalysts was close to 100%, irrespective of the reaction conditions. The benzaldehyde yield was usually obtained as the average of the yields at 2, 3, and 4 h time on stream (TOS).

3.1. Partial oxidation activity of Ag/SiO_2 catalysts

The dependencies of benzaldehyde and CO_2 yields on the reaction temperature over the Ag(1.0)/SiO_2 (Ag, 1.0 wt%) catalyst calcined at 773 K are illustrated in Fig. 1. The benzaldehyde yield increased significantly between 553 and 593 K. The CO_2 yield was very low in the range of temperatures studied (0.6% at 593 K). Thus the Ag/SiO_2 catalyst is effective for the selective partial oxidation of benzyl alcohol. The dependence of benzaldehyde yield on TOS was observed at reaction temperatures of 513 and 593 K (Fig. 2). In contrast to the behavior of the benzaldehyde yield versus TOS at 513 K, the benzaldehyde yield at 593 K increased with increasing process time in the initial stage of oxidation. This suggests that the supported Ag catalyst at 593 K is becoming more active in the induction period. XRD measurement of the Ag(1.0)/SiO_2 catalyst after the oxidation reaction at 593 K indicated a small peak of Ag(111) at $2\theta \approx 39^\circ$ in the catalyst, but the XRD pattern of the catalyst after the reaction at 519 K, as well as that of the fresh Ag(1.0)/SiO_2 catalyst, showed no corresponding peak (data not shown). Thus Ag metal particles seem to develop during the oxidation at higher reaction temperatures.

The effect of the benzaldehyde yield on the amount of Ag supported on SiO_2 was investigated at 513 K for catalysts calcined at 773 K. The catalytic activity was highly enhanced between 3 and 5 wt% Ag; benzaldehyde yields were 3.4, 7.1, and 31.6% by loadings of 1, 3, and 5 wt%, respectively.

The effect of the calcination temperature of the Ag(1.0)/SiO_2 catalyst on the benzaldehyde yield at the reaction temperature of 513 K was as follows: The benzaldehyde yields were 3.6, 6.5, and 49.9% and the BET surface areas were 297, 243, and 190 m^2/g for calcination temperatures of 773, 973, and 1173 K, respectively. Calcination at 1173 K caused a large increase in benzaldehyde yield despite the considerable decrease in the BET surface area. The XRD patterns of the Ag(1.0)/SiO_2 catalysts calcined at 773, 973, and 1173 K were compared to investigate the Ag state on the SiO_2 support. The XRD patterns of the catalysts calcined at 773 and 973 K showed no Ag metal peak, and were almost the same as that of SiO_2 support itself. In contrast, a small XRD peak at $2\theta = 39^\circ$ [Ag(111)] was observed in the catalyst calcined at 1173 K. Thus calcination at 1173 K apparently promotes the formation of metallic Ag on the SiO_2 support. To confirm the formation of Ag metal particles by calcination at high temperature, the effect of calcination temperature on benzaldehyde yield was investigated using the Ag(5.0)/SiO_2 catalyst. The Ag(5.0)/SiO_2 catalyst calcined at 1173 K had considerably greater catalytic activity (benzaldehyde yield, 84.7%) than the catalyst calcined at 773 K (benzaldehyde yield, 31.6%). Calcination of the Ag(5.0)/SiO_2 catalyst at 1173 K clearly caused the formation of Ag metal particles (Fig. 3b), in contrast to calcination at 773 K (Fig. 3a), which showed no Ag peaks. The size of the Ag metal particles esti-

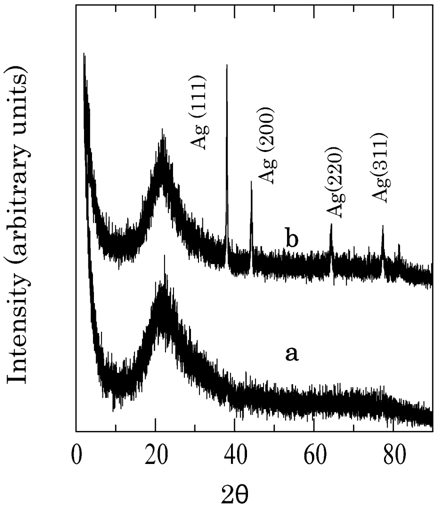


Fig. 3. XRD patterns of Ag(5.0)/SiO_2 catalysts. Calcined at (a) 773 and (b) 1173 K.

mated using Scherrer's equation was 76 nm. The Ag species supported on SiO_2 were thus confirmed to be Ag metal particles formed by calcining at high temperatures.

The oxidation of benzyl alcohol over the Ag(1.0)/SiO_2 catalyst precalcined at 1173 K, followed by reducing at 773 K for 5 h in flowing H_2 and then by calcining at 773 K, was compared with the results of the corresponding catalysts calcined at 1173 and 773 K. The benzaldehyde yields over both catalysts calcined at 1173 K (49.9%) and the catalyst calcined at 1173 K followed by reducing and once again calcining at 773 K (52.4%) were almost similar and much higher than that (3.5%) over the catalyst calcined at 773 K. In addition, the used Ag(1.0)/SiO_2 catalyst calcined at 1173 K after calcination at 773 K showed almost the same activity as the fresh catalyst. These results suggest that the Ag metal particles formed by calcination at 1173 K of the Ag(1.0)/SiO_2 catalyst are considerably stable and keep the Ag surface active during the oxidation of benzyl alcohol.

The effect of calcination atmosphere on the partial oxidation of benzyl alcohol was investigated at both 773 and 1173 K. Calcination of the Ag(1.0)/SiO_2 catalyst at 773 K caused no promotion of the activity, irrespective of the applied atmosphere. The benzaldehyde yields were 2.2% in N_2, 3.5% in H_2, and 3.5% in air. Calcination of the Ag(1.0)/SiO_2 catalyst at 1173 K in flowing N_2 had no effect on the activity of the partial oxidation (benzaldehyde yield, 2.3%), in contrast to a flowing air atmosphere (benzaldehyde yield, 49.4%). Calcination at high temperature in the presence of O_2 was necessary for the promotion of partial oxidation. The Ag_2O present in the supported Ag bulk of the Ag(1)/SiO_2 catalyst will decompose to Ag metal and gaseous O_2 at higher temperature in the presence of O_2. The oxidized Ag surface, which is thought to be responsible for the high activity of benzaldehyde formation, will be formed on the metallic Ag particle through an activated adsorption of O_2 at the high temperature of 1173 K.

Table 1
Influence of the support on the yield of benzaldehyde[a]

Support	Yield of benzaldehyde (%)
CaO	22.0
MgO	14.0
SiO_2	3.6
NaZSM-5	2.3
MCM-41	0.36
NaY	0.27

[a] Catalyst, Ag(1.0)/support, 0.2 g; calcination temperature (in flowing air), 773 K; reaction temperature, 513 K.

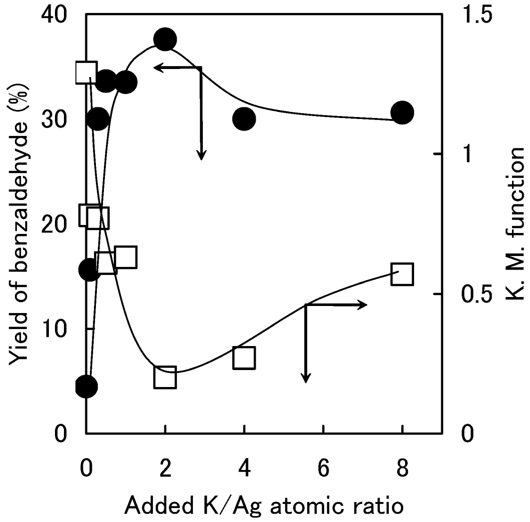


Fig. 4. Influence of added K/Ag atomic ratio on the yield of benzaldehyde and the K.M. function at around 400 nm. Catalyst, K-added Ag(1.0)/SiO_2 calcined at 773 K; reaction temperature, 513 K; $W/F = 8.70\ g_{cat}$ min/mol, W (catalyst weight) = 0.2 g, F (total mole flow rate) = 0.023 mol/min; N_2:O_2:benzyl alcohol = 32:3:1; ●, yield of benzaldehyde; □, maximum K.M. function at around 400 nm (a measure of metallic Ag, see text).

The effect of the support on benzaldehyde yield was investigated using MgO, CaO, MCM-41, NaZSM-5, and NaY, in addition to SiO_2 as summarized in Table 1. The selectivity for benzaldehyde was >99.5%, irrespective of the support. The alkaline earth supports MgO and CaO were effective for the partial oxidation of benzyl alcohol, but the zeolites were comparatively poor catalyst supports.

The effect of adding K to the Ag(1)/SiO_2 catalyst calcined at 773 K in flowing air on the benzaldehyde yield was investigated, because the basic supports CaO and MgO were superior supports for the partial oxidation. The dependence of the atomic ratio of added potassium to Ag on benzaldehyde yield was investigated at constant Ag amount (Fig. 4). Benzaldehyde yield sharply increased with a small increase in the K/Ag atomic ratio and reached a maximum at an atomic ratio of around 2. Potassium thus promoted the catalytic activity of Ag/SiO_2 for benzaldehyde formation. The effect of the calcination temperature of the K(2)/Ag(1.0)/SiO_2 with K/Ag atomic ratio = 2 on benzaldehyde yield is depicted in Fig. 5, together with the variation in the BET surface area of the catalyst. Ben-

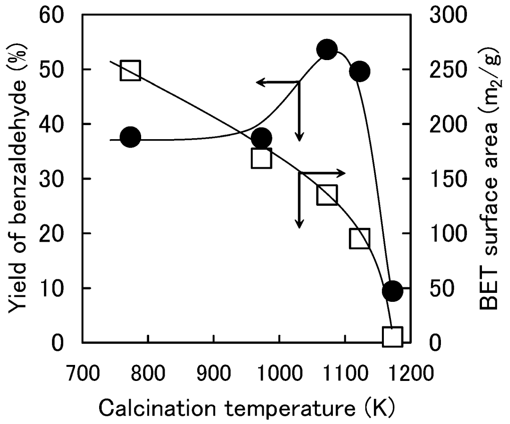


Fig. 5. Influence of calcination temperature of the K(2)/Ag(1.0)/SiO_2 catalyst on the yield of benzaldehyde and the BET surface area. Catalyst, K(2)/Ag(1.0)/SiO_2; calcination time, 5 h in flowing air; reaction temperature, 513 K; $W/F = 8.70$ g_{cat} min/mol, W (catalyst weight) = 0.2 g, F (total mole flow rate) = 0.023 mol/min; N_2:O_2:benzyl alcohol = 32:3:1; ●, yield of benzaldehyde; □, BET surface area.

zaldehyde yield was maximum at a calcination temperature of around 1100 K but declined sharply with further increases in calcination temperature. The sharp decrease in benzaldehyde yield was attributed to the decrease in the BET surface area of the catalyst. This result suggests that the K(2)/Ag(1.0)/SiO_2 catalyst is less heat-stable than the Ag(1.0)/SiO_2 catalyst, whose BET surface area was maintained at about 190 m^2/g even at a calcination temperature of 1173 K.

3.2. O_2 uptake of the reduced Ag/SiO_2 and the K-added counterpart

The O_2 uptake of the prereduced Ag(1.0)/SiO_2 catalyst calcined at 773 and 1173 K and of the prereduced K(2)/Ag(1.0)/SiO_2 catalyst calcined at 773 K were measured at 513 K to explore the capability of accommodating oxygen species. The O_2 uptake per Ag of the Ag(1.0)/SiO_2 catalyst calcined at 1173 K (0.022 O_2/Ag) and the K(2)/Ag(1.0)/SiO_2 catalyst calcined at 773 K were similar (0.023 O_2/Ag) and higher than that of the Ag(1.0)/SiO_2 catalyst calcined at 773 K (0.016 O_2/Ag). Thus calcination at high temperature and/or the addition of alkali metal thus are thought to make the interaction of the Ag/SiO_2 catalyst with O_2 more effective.

3.3. UV–vis DR spectra of the Ag/SiO_2 catalysts

The DR spectrum (Fig. 6a) of the Ag(1.0)/SiO_2 catalyst calcined at 773 K for 5 h under flowing air had two peaks at around 270 and 400 nm. The DR bands above 400 nm and around 320 nm of the Ag sample supported on SiO_2 were suggested [25] to be the plasma resonance absorption bands of Ag metal particles and Ag clusters, respectively. Ziyad et al. [26] reported that the DR bands at 270, 370, and 430 nm of $AgTh_2(PO_4)_3$ are due to silver particles of different sizes. In their studies on the pulse radiolytic reduction of Ag ions in aqueous solutions, Henglein et al. [27,28] attributed the absorption bands at around 280 and 330 nm to Ag_4^{2+} and Ag^5 clusters, respectively. More recently, the absorption spectra of Ag nanoparticles was reported to change significantly with a adsorbent, as the surface plasmon absorption spectrum of Ag nanoparticles depend on the nature and the concentration of adsorbed species [29]. Chen at al. [30] observed the red shift of the absorption spectra of Ag nanoplate solutions, of which absorption is due to the plasmon resonance, with the increased plate size. A significant red shift of the surface plasmon spectra of Ag was observed for increasing Ag nanoparticle arrays [31]. In the selective catalytic reduction (SCR) of NO by propane in the presence of hydrogen over Ag-MFI, the metallic Ag on the catalyst was reported to be oxidized to an $Ag_n^{\delta+}$ cluster during the SCR from the change in the UV–vis spectra [32]. The reduction of the Ag(1.0)/SiO_2 catalyst at 773 K for 5 h under flowing H_2 after calcination at 773 K under flowing air caused a large increase in the Ag plasmon peak at around 400 nm, with the peak at around 270 nm becoming comparatively small (Fig. 6b). The recalcination of the reduced catalyst at 773 K for 5 h under flowing air recovered the original DR spectrum (Fig. 6, c and a). Thus the treatment of the preoxidized Ag(1.0)/SiO_2 catalyst under H_2 filled the surface of the Ag/SiO_2 catalyst with reduced metallic Ag, and the reoxidizing treatment significantly decreased the amount of metallic Ag on the catalyst surface. The variation in the Ag plasmon peak at around 400 nm is thought to be a measure of the amount of metallic Ag present on the catalyst surface.

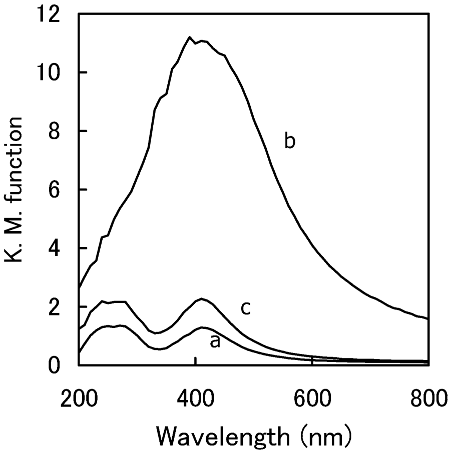


Fig. 6. DR spectra of Ag(1.0)/SiO_2 catalysts treated under various conditions. (a) Calcined at 773 K for 5 h in flowing air; (b) after (a), reduced at 773 K for 5 h in flowing H_2; (c) after (b), calcined again at 773 K for 5 h in flowing air.

Fig. 7 illustrates the DR spectra of the Ag(1.0)/SiO_2 catalysts calcined at different temperatures in flowing air. The intensity of the Ag plasmon peak at around 400 nm decreased with increasing calcination temperature. This indicates that calcination at 773 K maintains the catalyst surface in the metallic state, but the surface of the Ag/SiO_2 catalyst calcined at 1173 K consists of oxidized Ag, rather than reduced

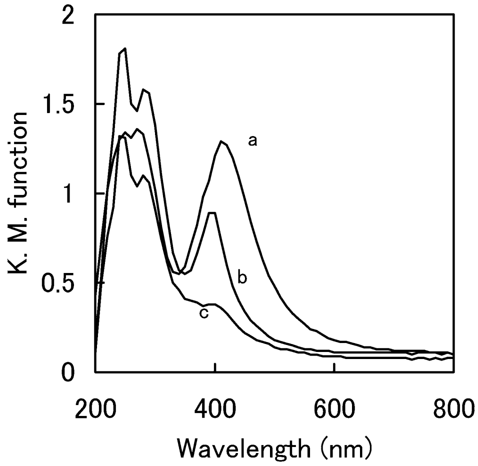


Fig. 7. DR spectra of the Ag(1.0)/SiO_2 catalysts calcined at different temperatures. Calcination time, 5 h in flowing air; (a) calcined at 773 K; (b) calcined at 973 K; (c) calcined at 1173 K.

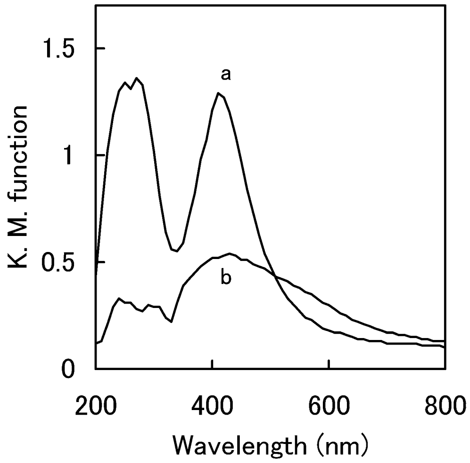


Fig. 8. DR spectra of the Ag(1.0)/SiO_2 and the Ag(1.0)/CaO catalysts. After calcination at 773 K for 5 h in flowing air; (a) Ag(1.0)/SiO_2; (b) Ag(1.0)/CaO.

metallic Ag. The formation of the oxidized Ag surface is due to an activated adsorption of O_2 on the metallic Ag particle at a high calcination temperature, as previously stated.

The DR spectra of the Ag(1.0)/CaO and the Ag(1.0)/SiO_2 catalysts calcined at 773 K in flowing air are illustrated in Fig. 8. The Ag plasmon peak at around 400 nm of the Ag(1.0)/CaO catalyst considerably broadened toward longer wavelengths, and its peak intensity at around 400 nm was lower than that of the Ag(1.0)/SiO_2 catalyst. This may suggest [30,31] that the distribution of metallic Ag particle sizes on the CaO support shifts toward larger metallic Ag particles than on the SiO_2 support and that the Ag surface of the metallic Ag bulk supported on the CaO is more easily oxidized than that of the Ag/SiO_2, although the XRD peaks due to metallic Ag particles were not detected in the Ag(1.0)/CaO or the Ag(1.0)/SiO_2 catalyst. The basic CaO support is thought to make the supported Ag bulk more easily reduced to metallic Ag due to electron donation from the CaO to the Ag bulk. The surface of the resulting metallic Ag particle is able to interact with gaseous O_2 more easily than the surface of the Ag bulk containing Ag_2O supported on SiO_2. The surface of the Ag metallic bulk is thus oxidized more easily on the CaO support than on the SiO_2 support, even at a comparatively low calcination temperature of 773 K. The significantly higher catalytic activity of the Ag(1.0)/CaO catalyst compared with the Ag(1.0)/SiO_2 is thought to be due to the oxidized Ag species on the surface of the catalyst.

Fig. 4 (☐) illustrates the variation in the intensity of the Ag plasmon peak at around 400 nm of the K/Ag(1.0)/SiO_2 catalyst on the K/Ag atomic ratio. The intensity of the Ag plasmon peak at around 400 nm, the measure of the surface metallic Ag, had a minimum at the K/Ag atomic ratio of 2 and tended to increase at an atomic ratio >2. In contrast, the benzaldehyde yield (Fig. 4, ●) passed through a maximum at the atomic ratio of 2. The correlation obtained between the benzaldehyde yield and the intensity of the Ag plasmon peak, which is thought to be a measure of the metallic Ag present on the surface of the catalyst, can be interpreted as follows. The oxidized and/or the oxygenated Ag species, being responsible to the partial oxidation of benzyl alcohol, had a maximum on the surface of the K/Ag(1.0)/SiO_2 catalyst at the atomic ratio of 2, because the amount of metallic Ag species on the surface was at a minimum at a K/Ag atomic ratio of 2. The added K is thought to promote the formation of the oxidized Ag on the surface of the catalyst, although excessive K tended to inhibit the oxidation activity.

3.4. *EXAFS spectra of Ag/SiO_2 catalysts*

A set of 5 wt% Ag samples, instead of the corresponding 1 wt% Ag samples, was used for EXAFS measurement to obtain clear-cut EXAFS data. Fig. 9a–f illustrates the EXAFS data (Ag K-edge EXAFS Fourier transforms) of the Ag(5.0)/SiO_2 calcined at 773 and 1173 K for 5 h in flowing air, the K(2)/Ag(5.0)/SiO_2 calcined at 773 K, and the Ag(5.0)/CaO calcined at 773 K, together with the those of Ag foil and Ag_2O as references. The EXAFS of the Ag foil (Fig. 9a) contains a dominant contribution from Ag nearest neighbors at 2.75 Å. The EXAFS of the Ag_2O reference (Fig. 9b) shows a main contribution from Ag–O in the first shell at 1.69 Å and a minor one from Ag–O–Ag in the second shell at 3.22 Å. The Ag K-edge EXAFS of the Ag/SiO_2 catalyst calcined at 773 K (Fig. 9c) reveals a contribution from Ag–O (1.69 Å), in addition to a shell at 2.76 Å due to Ag nearest neighbors. The Ag–O peak was tentatively assumed to be due to a presence of Ag_2O from the precalcination treatment of the catalyst, although the possibility of the formation of amorphous silver silicate cannot be denied [33,34]. However, the Ag K-edge EXAFS Fourier transform of the Ag/SiO_2 catalyst calcined at 1173 K (Fig. 9d) was almost the same as the reference Ag foil. This indicates that the calcination temperature of the Ag/SiO_2 significantly af-

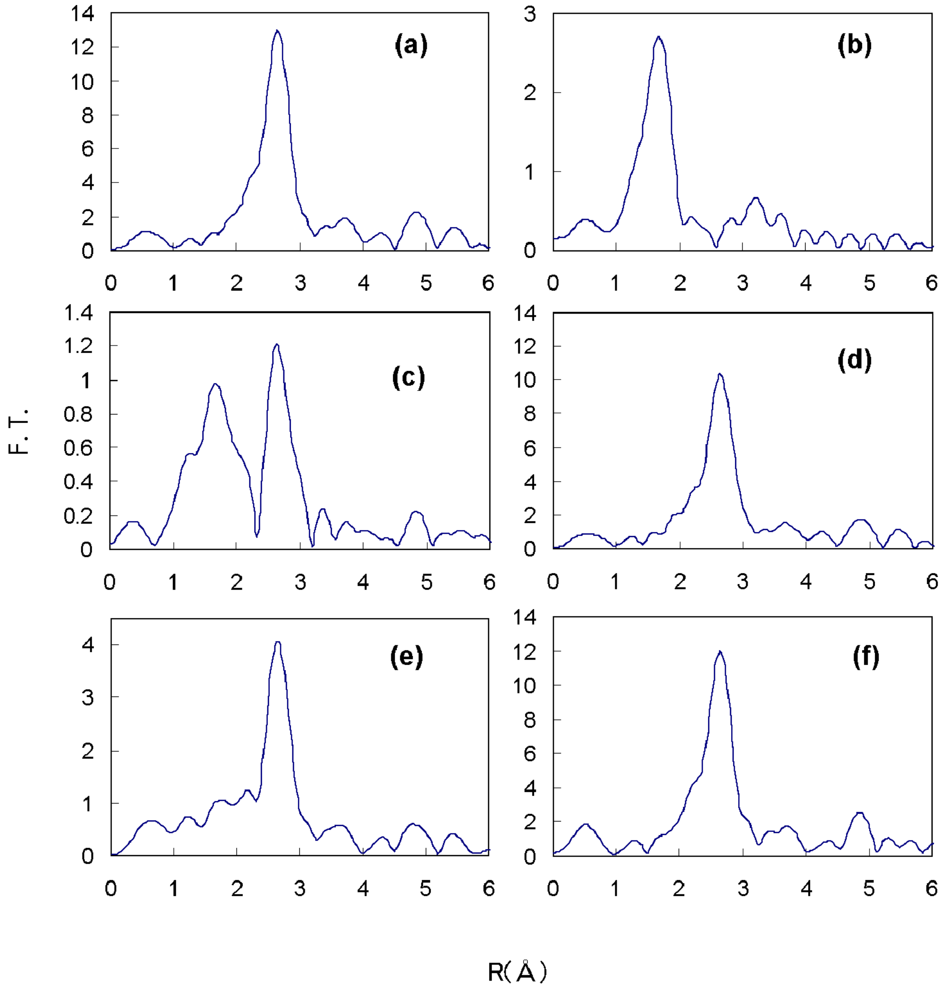


Fig. 9. XAFS spectra. (a) Reference Ag foil; (b) reference Ag_2O powder; (c) Ag(5.0)/SiO_2 calcined at 773 K for 5 h in flowing air; (d) Ag(5.0)/SiO_2 calcined at 1173 K for 5 h in flowing air; (e) K(2)/Ag(5.0)/SiO_2 calcined at 773 K for 5 h in flowing air; (f) Ag(5.0)/CaO calcined at 773 K for 5 h in flowing air.

fected the state of Ag supported on SiO_2; thus the calcination at high temperature of the Ag/SiO_2 led to metallic Ag, in good agreement with the XRD results (Fig. 3). Calcination at high temperature (1173 K) thus made the bulk Ag more reducible. Ag_2O in the supported Ag particle will decompose to Ag and O_2 at higher temperatures to form metallic Ag bulk. EXAFS of the K/Ag/SiO_2 calcined at 773 K (Fig. 9e) had a Ag–Ag shell at 2.76 Å, which has a position similar to that of the Ag foil. The Ag/CaO calcined at 773 K (Fig. 9f) showed a EXAFS peak at 2.75 Å, which is again the same as that of the Ag foil. The addition of alkali metal and use of a basic support enhanced the reduction of the supported Ag even at low calcination temperature (773 K).

The Ag/SiO_2 calcined at 773 K contained considerable Ag_2O, in addition to Ag metal. In contrast, the Ag/SiO_2 calcined at 1173 K, the K/Ag/SiO_2 calcined at 773 K, and the Ag/CaO calcined at 773 K were found to be composed mainly of Ag metal. All three of these catalysts had greater catalytic activity for the partial oxidation of benzyl alcohol than that of the Ag/SiO_2 calcined at 773 K. The results obtained from the catalytic activity, the DR spectra, and EXAFS indicate that the Ag bulk supported on the CaO consists mainly of metallic Ag, rather than Ag_2O, of which metallic Ag bulk is responsible for oxidizing the Ag surface. The oxidized Ag surface is thought to play vital role for the partial oxidation of benzyl alcohol.

4. Discussion

The reaction temperature had a significant effect on the catalytic activity of the benzyl alcohol oxidation using the Ag/SiO_2 catalyst calcined at 773 K (Fig. 1). The presence of an induction period at the reaction temperature of 593 K (Fig. 2) suggests that the supported Ag bulk, including Ag_2O, of the Ag/SiO_2 catalyst is becoming metallic Ag at the initial stage, and that oxygen molecules adsorbed on the metallic Ag is activating to form an oxidized Ag surface, the surface species of which are thought to be active for the partial oxidation of benzyl alcohol. The low benzaldehyde yield at reaction temperatures <553 K may be caused by the inhibition of metallic Ag bulk formation and the activated oxygen adsorption at the lower reaction temperature.

Calcination of the Ag(1.0)/SiO_2 catalyst at 1173 K *in the presence of O_2* caused a sharp increase in the benzaldehyde yield even at the comparatively low reaction temperature of 513 K. However, the benzaldehyde yield did not increase over that of the Ag(1.0)/SiO_2 catalyst calcined at 1173 K *in the absence of O_2*. Calcination of the Ag(5.0)/SiO_2 catalyst at 1173 K in flowing air allowed the supported bulk Ag to be reduced to metallic Ag species (Fig. 3). The EXAFS spectrum of the Ag(5.0)/SiO_2 catalyst calcined at 1173 K in flowing air indicated that the Ag is substantially present as metallic Ag, whereas the catalyst calcined at 773 K in air contains a considerable amount of Ag_2O species in addition to metallic Ag. From these results, we can deduce that calcination of the Ag/SiO_2 catalyst at a high temperature (e.g., 1173 K) in air causes the Ag_2O to be converted to metallic Ag. O_2 at 1173 K may play a role of relocating the small Ag_2O to form large Ag_2O particles, which are easier to reduce. The resulting metallic Ag species promote the affinity of the Ag surface with gaseous O_2, and the generated oxidized and/or oxygenated Ag surface is thought to be active for the partial oxidation of benzyl alcohol. The increase in O_2 uptake of the prereduced Ag(1.0)/SiO_2 catalyst calcined at 1173 K supports this deduction. In addition, the decline in the Ag plasmon spectrum of the Ag(1.0)/SiO_2 catalyst calcined at 1173 K (Fig. 7) suggests that the surfaces of the metallic Ag particles are oxidized, rather than metallic.

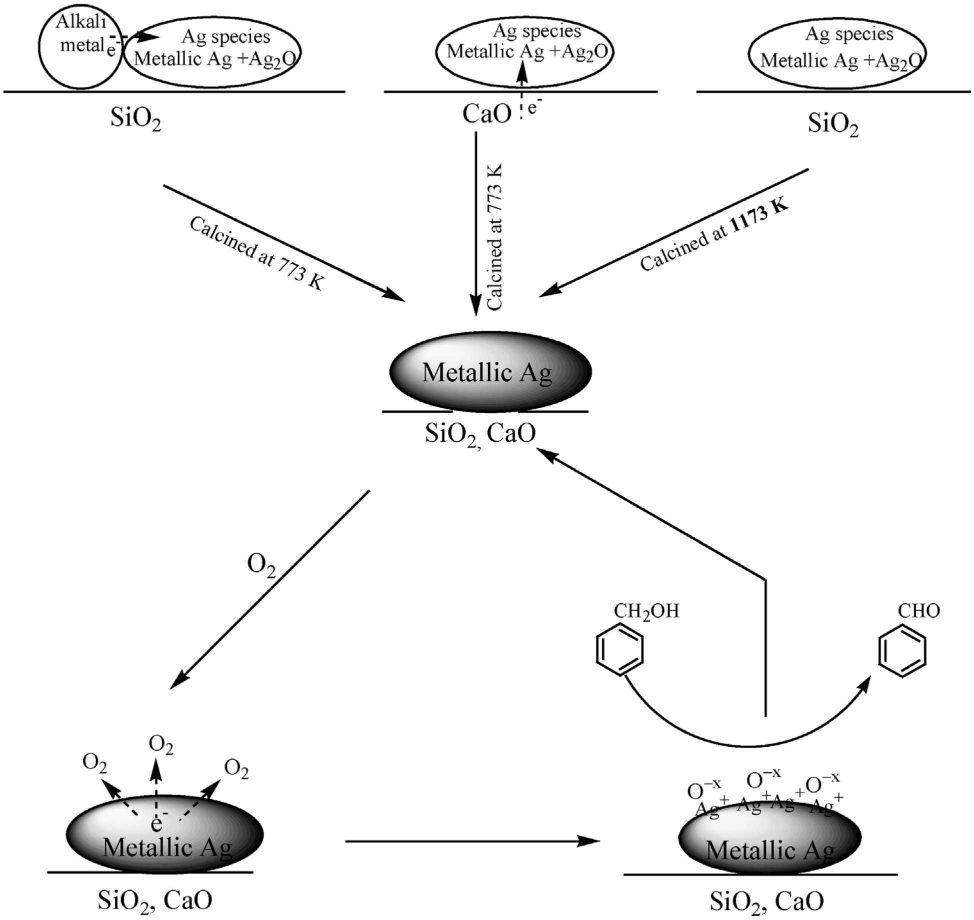
The Ag impregnated on a basic support such as CaO exhibited high oxidation activity even when the Ag(1.0)/CaO catalyst was calcined at the comparatively lower temperature of 773 K (Table 1). The potassium added to the Ag(1.0)/SiO_2 catalyst promoted the catalytic activity for benzaldehyde formation (Fig. 4). Calcination of the K(2)/Ag(1.0)/SiO_2 catalyst at the higher temperatures also promoted oxidation activity, although an excessive calcination temperature decreased the benzaldehyde yield because of the sharp decline in the BET surface area (Fig. 5). The comparison of the Ag plasmon peaks of Ag(1.0)/SiO_2 and Ag(1.0)/CaO (Fig. 8) suggests that the Ag surface of the latter catalyst is more oxidized by O_2 than the former. The KM functions at 400 nm of the K/Ag(1.0)/SiO_2 catalysts were plotted against the added K/Ag atomic ratio (Fig. 4). The variation in the KM function is thought to be a measure of the surface metallic Ag—in other words, a measure of the oxidized Ag surface, as suggested in Section 3. Thus a clear correlation between the benzaldehyde yield and the oxidized Ag surface (Fig. 4) was confirmed. The increase in the O_2 uptake of the prereduced K(2)/Ag(1.0)/SiO_2 catalyst compared with that of the Ag(1.0)/SiO_2 catalyst also agrees with the results of the DR spectra. EXAFS of the Ag(5.0)/CaO and the K(2)/Ag(5.0)/SiO_2 catalysts calcined at 773 K indicated that both of the supported Ag bulk components were substantially metallic Ag, in contrast with that of the Ag(5.0)/SiO_2 calcined at 773 K, of which the bulk Ag contains Ag_2O in addition to metallic Ag (Figs. 9c, 9e, and 9f). The role of the basic support or the added alkali metal is to reduce the supported Ag bulk to form metallic Ag through electron donation. The surface of the resulting metallic Ag will interact more easily with gaseous oxygen, followed by the formation of an oxidized Ag surface. Furthermore, the added alkali metal or the basic support will activate the adsorbed oxygen molecule by donating electrons to the adsorbed oxygen molecules through the Ag bulk and dissociating to atomic oxygen species.

The results of this study support that calcination at high temperature in the presence of oxygen, a basic support, and the addition of alkali metal promote the reduction of the supported Ag species to form metallic Ag. The surface of the metallic Ag particles has a higher affinity for gaseous oxygen than the mostly oxidized Ag particles. The formed surface atomic oxygen species in contact with the metallic Ag bulk are probably more active than atomic oxygen species neighboring Ag^+ cations in fully oxidized oxide (Ag_2O) particles. Using a physical mixture consisting of 10 wt% Ag_2O and SiO_2 as a catalyst at a reaction temperature of 513 K, the benzaldehyde yield was only 2%. The high catalytic activity of the supported Ag catalysts treated at as high calcination temperature, using CaO as a support, or added alkali metal, indicate that the oxidized Ag surface formed on the metallic Ag particle is responsible for the partial oxidation of benzyl alcohol. Atomic oxygen species on the Ag(110) surface were detected at around 600 K from a temperature-programmed desorption profile [35]. Barteau et al. [10–12] demonstrated that ethylene oxide adsorbed on Ag(111) undergoes ring opening to produce a stable surface oxametallacycle consisting of Ag, atomic oxygen, and ethylene group, of which surface intermediate reacting at 300 K to reform ethylene oxide. The oxygen species present on the Ag surface of the supported Ag catalysts used in this study are thought be atomic states, because the molecular oxygen species are dissociated to the corresponding atomic ones through electron transfer from the electron-rich metallic Ag particles.

A schematic model of the active sites of the supported Ag catalyst is drawn in accordance with the aforementioned considerations (Scheme 1). Addition of alkali metal, an alkali earth metal oxide support, or calcination at higher temperature brings the supported Ag species to the metallic state. Gaseous oxygen molecule interacts with the Ag surface through electron transfer from the electron-rich metallic Ag bulk to the O_2, followed by the formation of atomic oxygen species such as $O_{ad}{}^{-x}$. The surface Ag species will be positive-charged Ag species, although the bulk is metallic Ag. The adsorbed atomic oxygen with nucleophilic character formed will activate the C–H bond of benzyl alcohol to produce corresponding aldehyde.

5. Conclusion

The partial oxidation activity of SiO_2-supported Ag catalysts was studied using the gas phase catalytic oxidation of benzyl alcohol. The effects of the calcination temperature,



Scheme 1.

the support, and the addition of alkali metal on benzaldehyde yield were investigated at a comparatively low reaction temperature. Treatment at high calcination temperature, use of a basic support, and the addition of alkali metal significantly promoted the catalytic activity of the supported Ag catalyst for the partial oxidation. A comparison of XRD and/or EXAFS findings for the original Ag/SiO_2 and the supported Ag counterparts modified by a high calcination temperature, use of a basic support, or addition of an alkali metal supported that these modifications of the Ag/SiO_2 catalyst made the bulk of the supported Ag reduce more readily to form metallic Ag species. The resulting metallic Ag seems to have a higher affinity for gaseous O_2, in agreement with the comparison of the O_2 uptake and the DR spectra of both the original Ag/SiO_2 catalyst and the modified counterparts. The oxidized Ag surface on the supported metallic Ag was proposed to be an active site for the partial oxidation of benzyl alcohol. A schematic model of the formation of the active Ag sites was proposed based on the results.

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