Oxidative decomposition of formaldehyde on silver–cerium composite oxide catalyst

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Silver–cerium composite oxide was active for low temperature oxidative decomposition of formaldehyde. Its high activity was due partly to the high dispersion of active silver on the CeO_2. The surface oxygen of this composite catalyst was removed more easily than those on single component Ag_2O or CeO_2, which also seemed to contribute to the high activity of this catalyst. IR analysis revealed that formaldehyde was decomposed both on silver–cerium composite catalyst and CeO_2 in the presence of oxygen to produce methoxide, dioxymethylene, and/or polyoxymethylene even at room temperature. In addition bi-carbonate was formed on silver–cerium composite catalyst and formate was produced on CeO_2. These intermediates suffered further oxidation at higher temperatures (373 and 423 K) easily on silver–cerium composite catalyst, whereas degradation of them was rather difficult on CeO_2.

Keywords: Formaldehyde; oxidative decomposition; Ag/Ce composite catalyst

1. Introduction

In 1984 the Environmental Protection Agency decided to list formaldehyde as a priority chemical for regulatory assessment under the Toxic Substance Control Act [1]. The decision was made because formaldehyde is carcinogenic and its detrimental effect on the environment will be serious as the number of the methanol-fueled vehicles will increase in the future. We are exposed to formaldehyde in daily life even now; e.g., it is contained in cigarette smoke and is found as a residual in

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various consumer products such as formaldehyde-based resins and cosmetics. Thus detoxification of it seems to be an interesting object of research. Previously we found that formaldehyde is readily decomposed by ruthenium supported on CeO_2 in an aqueous phase [2]. This catalyst is also effective in the vapor phase combustion of formaldehyde [3]. However, as ruthenium is rather expensive, development of cheaper catalysts is desirable. Silver is more abundant and less expensive than group VIII precious metals; however, it is unstable against heat and aggregates at high temperatures and, thus, it cannot be used in the usual combustion reactions. When reactions do not require high temperatures such as that of the oxidation of carbon monoxide, silver exhibits high activity and durability [4]. As formaldehyde is fragile enough and is readily decomposed at low temperatures [2,3], silver is expected to act as an effective catalyst for its detoxification. CeO_2 is an efficient support for combustion catalysts [5–7], and we also found its high promoting effect on the oxidizing activity of manganese(III) oxide [8,9]. Thus we investigated the oxidative decomposition of formaldehyde on silver supported on CeO_2.

2. Experimental

2.1. PREPARATION OF THE CATALYSTS

Silver–cerium composite oxide was prepared by coprecipitation method. Aqueous NaOH (3 N) was added to an aqueous solution of known amounts of silver(I) nitrate and cerium(III) nitrate until the pH of the solution was about 10. The resultant precipitate was washed with deionized water three times, and it was dried at 373 K overnight, followed by calcination at 573 K in air for 3 h. Ag_2O, Co_3O_4, Mn_2O_3, CeO_2, NiO, CuO, and Fe_2O_3 were prepared by precipitation from an aqueous solution of the corresponding nitrates according to the same procedure as above. The calcination temperature was 773 K except for Ag_2O (573 K). These catalysts were pressed into a disc under a pressure of 20 MPa and were cut to 8–14 mesh-size before use.

2.2. APPARATUS AND PROCEDURE

Reactions were carried out under an atmospheric pressure with an ordinary tubular flow reactor (inner diameter of the quartz reaction tube: 6 mm). 1 ml of the catalysts was charged into the reactor, and the reactor was heated with an electric furnace. Aqueous formaldehyde containing methanol as a stabilizer was fed into the reactor by use of an automatically driven syringe under a flow of air. The composition of the reaction gas mixture was formaldehyde: 0.42%, methanol: 0.074%, H_2O: 19.9%, N_2: 62.7%, and O_2: 16.9%. The space velocity of this reaction gas was 21000 h^{-1}. The reaction was carried out at 423, 473, 523, and 573 K: the reaction below 423 K was not examined because the temperature of the catalyst bed fluctuated due to condensation of water. Formaldehyde which escaped decomposition was monitored at the exit of the reactor. The reaction was not affected by mass transfer limitation because the conversion of formaldehyde at 423 K was independent of the particle size of Co_3O_4 and silver–cerium composite oxide with a Ag to Ce molar ratio of 5/95.

Temperature-programmed desorption (TPD) of oxygen was carried out with a quartz sample tube connected to an ordinary vacuum line and to a thermal conductivity detector. The catalysts were charged into the sample tube and were heated at 523 K for 1 h under a flow of oxygen. Then they were cooled down to room temperature in oxygen, followed by evacuation. Then the catalysts were again heated at a rate of 5 K/min under a flow of He (35 ml/min), and the desorbed oxygen was monitored.

2.3. ANALYSIS

Formaldehyde which escaped decomposition was absorbed in a cold water trap (273 K) for 30 min and was analyzed by an iodometric titration as follows. 2 N NaOH and an excess amount of aqueous I_2 were added to an aliquot of the above formaldehyde solution, and the mixture was kept standing for 10 min in the dark. After the solution was acidified with 2 N HCl, the remaining I_2 was titrated with 0.1 N aqueous thiosulfate.

X-ray diffraction patterns, ESCA spectra, and IR spectra were obtained by the use of a Rigaku Denki 2012 geigerflex, a Shimadzu ESCA 750 spectrophotometer, and a JASCO FTIR-5MP infrared spectrophotometer equipped with a diffuse reflectance cell, respectively.

3. Results and discussion

Table 1 shows the result of the decomposition of formaldehyde on various catalysts together with their BET surface areas. Formaldehyde is fragile and can be decomposed by these catalysts at relatively low temperatures. 100% of conversion was attained at 473 K on Co_3O_4, and NiO decomposed 98.5% of formaldehyde at 523 K. Although Ag_2O had moderate activity among the catalysts examined, its inherent activity seems high considering its small surface area (1.9 m^2/g). The activity of CeO_2 was rather low, especially, at high temperatures (523 and 573 K). On combining silver and cerium, high activity appeared and 100% of conversion was attained at 523 K for all silver–cerium composite catalysts irrespective of their composition. One noted feature of them is that they exhibited high activity at low temperature (423 K) compared with other catalysts; the conversion exceeded 80%, whereas other catalysts decomposed less than 62% of formaldehyde at that temperature.

One of the reasons for the high activity of the silver–cerium composite catalysts

Table 1

Oxidative decomposition of formaldehyde. [catalyst] = 1 ml; reaction gas = formaldehyde 0.42%, methanol 0.074%, H_2O 19.9%, N_2 62.7%, O_2 16.9%; SV = 21000 h^{-1}

Catalyst	SW[a] (m^2/g)	Conversion (%)			
		423 K	473 K	523 K	573 K
Ag/CeO$_2$(50/50)[b]	40.5	95.5	100	100	100
Ag/CeO$_2$(20/80)[b]	54.3	94.7	97.8	100	100
Ag/CeO$_2$(10/90)[b]	76.4	83.4	91.4	100	100
Ag/CeO$_2$(5/95)[b]	84.4	81.9	96.7	100	100
Ag_2O	1.9	60.4	92.8	91.0	98.0
CeO_2	76.7	54.3	56.7	61.3	79.3
Co_3O_4	45.7	56.0	100	100	100
NiO	91.0	61.9	90.8	98.5	100
CuO	29.8	54.4	64.5	84.1	100
Mn_2O_3	22.9	45.7	43.3	91.3	100
Fe_2O_3	76.2	17.8	19.9	63.8	91.1

[a] BET surface area.

[b] Molar ratio.

seems to be due to the increased dispersion of the inherently active Ag as shown by the high surface areas of the composite catalysts (see table 1). This situation is shown by the X-ray diffraction analysis of a silver–cerium composite catalyst with a Ag to Ce molar ratio of 20/80 [Ag/CeO$_2$(20/80)] (fig. 1). The X-ray diffraction

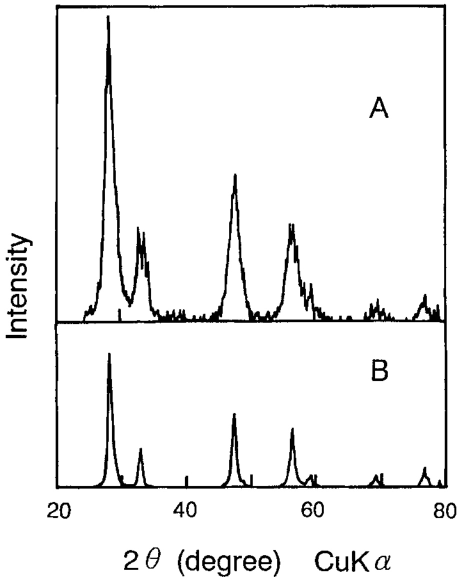

Fig. 1. X-ray diffraction patterns of (A) Ag/CeO$_2$(20/80) calcined at 573 K and (B) CeO$_2$ calcined at 573 K. The intensity of the diffraction peaks of Ag/CeO$_2$(20/80) is amplified by a factor of 10.

pattern of Ag/CeO$_2$(20/80) exactly coincided with that of the original CeO$_2$ although less resolved, and no peak due to Ag species was observed: silver species are highly dispersed without forming any appreciably large grains.

In order to see the state of Ag, ESCA analysis was carried out. Ag$_2$O showed an MNN Auger peak at 903.0 eV, and metallic Ag had a peak at 901.5 eV. The MNN Auger peak of Ag for Ag/CeO$_2$(20/80) calcined at 573 K appeared at the position between these two peaks (902.2 eV). It is known that CeO$_2$ helps to retain the reduced state of the supported precious metals [10], and we also observed that manganese(III) oxide is quite easily reduced on mere contact with CeO$_2$ at a temperature as low as 423 K [8]. Thus the silver species present in the present composite catalyst (calcined at 573 K) seems to be in the form of partially reduced Ag$_2$O. The surface composition of Ag/CeO$_2$(20/80) calcined at 573 K as determined by ESCA technique was Ag: 31.9 mol% and Ce: 68.1 mol%, showing an enrichment of Ag on the surface.

As mobility of oxygen is thought to be one factor affecting the activity of combustion catalysts [4], desorption of oxygen from Ag/CeO$_2$(20/80) was monitored by TPD technique (fig. 2). The TPD curves for the same amounts (moles) of Ag$_2$O and CeO$_2$ which were contained in Ag/CeO$_2$(20/80) were also observed. In this case the form of Ag in Ag/CeO$_2$(20/80) was tentatively assumed as Ag$_2$O although ESCA analysis revealed that the Ag was present as a slightly reduced state of Ag$_2$O. Ag$_2$O had a sharp desorption peak of oxygen above 700 K which caused the change from Ag$_2$O to metallic Ag, and CeO$_2$ showed a broad but indistinct peak in the wide temperature range. Ag/CeO$_2$(20/80) released the oxygen which seemed to come from both CeO$_2$ and Ag$_2$O (a peak around 700 K). However, the amount of oxygen desorbed from Ag/Ce(20/80) was much larger than the sum of the de-

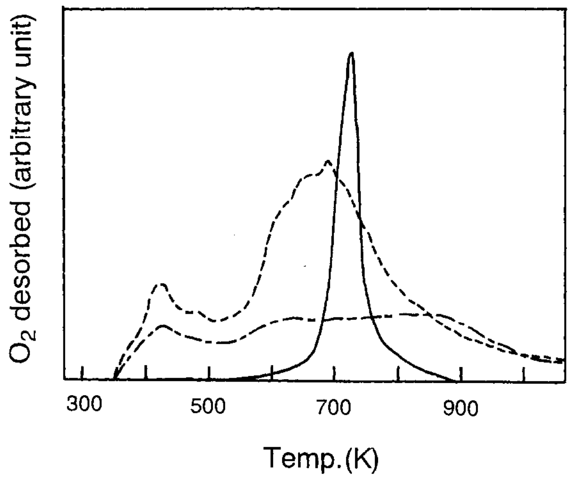

Fig. 2. TPD of oxygen from CeO$_2$ (– – –), Ag$_2$O (——) and Ag/CeO$_2$(20/80) (- - -). The same amounts (moles) of Ag$_2$O and CeO$_2$ which correspond to those in Ag/CeO$_2$(20/80) were used.

sorbed oxygen from Ag_2O and CeO_2; the latter is 2.14 times the former. Especially, the desorption of the oxygen which seemed to belong to CeO_2 was stimulated in the presence of Ag at low temperature region. This activation of oxygen seems to play one important role to induce high combustion activity of this composite catalyst at low temperatures [4].

Fig. 3 shows the results of the IR analyses. Paraformaldehyde was heated under a flow of nitrogen and the resultant formaldehyde (3.6%) was introduced over the catalysts for 30 min at room temperature. When formaldehyde adsorbed on Ag/ CeO_2(20/80) was exposed to oxygen for 10 min at room temperature, absorption bands were observed at 3000–2800 (typically 2917), 1616, 1380, and 1150–1050 (typically 1116 and 1099) cm^{-1} regions, which hereafter will be referred to as A, B, C, and D, respectively (spectrum 1). Bands A and D were assumed to be due to C–H stretching and C–O stretching vibrations of methoxide, dioxymethylene, and/or polyoxymethylene, respectively [11]. These bands disappeared at 373 K under oxygen atmosphere, while bands B and C remained unchanged (spectrum 2). As species showing absorption bands B and C did not have C–H bond (band A), both bands were assigned as due to bi-carbonate species from literature data [12]. The former band is due to a $C\overset{...}{-}O$ asymmetric stretching vibration and the latter to a $C\overset{...}{-}O$ symmetric stretching vibration of bi-carbonate species, respectively. All

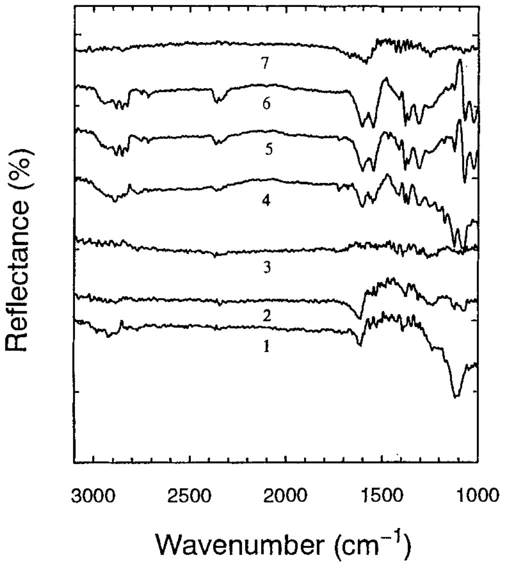

Fig. 3. IR spectra of adsorbed species on the catalysts. Formaldehyde in nitrogen (3.6%) was adsorbed on the catalysts for 30 min, followed by introduction of oxygen at prescribed temperatures for 10 min. A unit scale of the ordinate corresponds to 50% of reflectance. (1) Ag/CeO_2, room temperature; (2) Ag/CeO_2, 373 K; (3) Ag/CeO_2, 423 K; (4) CeO_2, room temperature; (5) CeO_2, 373 K; (6) CeO_2, 473 K; (7) after 150 ml of CO_2 was passed over Ag/CeO_2(20/80) at room temperature under oxygen flow, oxygen was further introduced for 20 min.

the bands disappeared at 423 K in oxygen (spectrum 3). As a comparison CO_2 gas was adsorbed on Ag/CeO_2(20/80) and treated with oxygen for 20 min at room temperature. It showed absorption bands at 1584 and 1252 cm^{-1} due to bidentate carbonate [13] (spectrum 7). Models of bi-carbonate and bidentate carbonate are shown in fig. 4.

Formaldehyde was introduced onto CeO_2 and was treated in the same way. After the treatment with oxygen for 10 min at room temperature, absorption bands were observed at 3000–2800 (typically 2942, 2882, 2851, and 2824), 1650–1500 (typically 1603 and 1541), 1450–1300 (typically 1414, 1381, 1360, and 1306), and 1150–1050 cm^{-1} (typically 1123 and 1069) cm^{-1} regions, which hereafter will be referred to as A', B', C' and D', respectively (fig. 3, spectrum 4). A band at 2350 cm^{-1} was due to CO_2 in the atmosphere. Band D' disappeared at 373 K (spectrum 5): although the noise in this region did not give the conclusive evidence of its disappearance, the same experiment on CeO_2 carried out in the previous work showed that this band disappeared under the same reaction condition [3]. Band D' observed at room temperature seems to be due to C–O stretching vibration of methoxide, dioxymethylene, and/or polyoxymethylene. Corresponding C–H stretching vibration of these species was observed in the A' region though this region also included absorption band due to formate species described below. Bands A', B', and C' observed above 373 K (spectra 5 and 6) were assumed to be due to C–H stretching, C=O asymmetric stretching, and C=O symmetric stretching vibrations of formate, respectively [11]. As bands B' and C' are complex, CO_3 or CO_2 species without C–H bond (e.g. bi-carbonate or bidentate carbonate) may be present [14]. Formate species was already present at room temperature (spectrum 4). It seems natural to deduce that methoxide, dioxymethylene, and/or polyoxymethylene present at room temperature suffered further oxidation to form formate at 373 K: intensity of bands A', B' and C' due to formate increased with temperature increase (compare spectra 5 and 6 with spectrum 4).

Comparison of the result on Ag/CeO_2(20/80) with that on CeO_2 shows that the former catalyst produced more deeply oxidized species (bi-carbonate) than the latter (formate) at room temperature. In addition all species are removed on Ag/

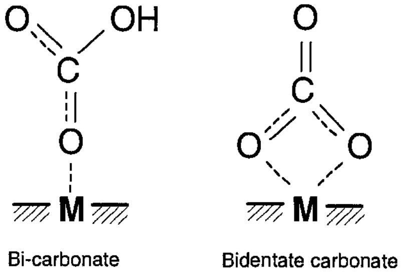

Fig. 4. Schematic models of bi-carbonate and bidentate carbonate species.

CeO_2(20/80) at 423 K (spectrum 3), whereas further oxidation did not take place on CeO_2 at that temperature (compare spectrum 5 with spectrum 6). These results showed that formaldehyde is oxidized more easily on silver–cerium composite oxide than on CeO_2, which well explained the higher activity of the silver–cerium composite catalyst. Silver–cerium composite catalyst decomposes formaldehyde easily even at room temperature (spectrum 1). However, as shown by the spectra 2 and 3, further oxidation occurred at 423 K. Thus for the reaction to proceed at an appreciable rate, the reaction temperature needs to be maintained above 423 K.

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