Catalysis Today 153 (2010) 133–135

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Catalytic soot combustion over CeO_2-based oxides

Hiroki Muroyama, Shigeki Hano, Toshiaki Matsui, Koichi Eguchi*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

ARTICLE INFO

Keywords:
Soot combustion
CeO_2
Reducibility
Surface area

ABSTRACT

The catalytic soot combustion, surface area, and reducibility for the CeO_2-based oxides were investigated. The carbon black (CB), which was used as a model of soot particle, was combusted over 700 °C, while the CeO_2-based catalysts reduced the CB oxidation temperature by more than 150 °C. Although the addition of rare-earth metal oxides to CeO_2 increased the surface area, no remarkable improvement of catalytic activity was confirmed. The transition metal oxide added to CeO_2 significantly promoted the oxidation reaction, and the CuO–CeO_2 catalyst exhibited the highest activity despite the lowest surface area of all composite oxides investigated. The reduction behavior of catalysts was closely related with the activity of CB oxidation. It was indicated that the oxygen species available for the oxidation reaction was increased by the addition of transition metal components. When the Cu content was varied for the CuO–CeO_2 catalyst, the optimal amount existed for the CB oxidation.

1. Introduction

The heavy reliance on fossil fuel has significantly increased the atmospheric concentration of carbon dioxide (CO_2), giving rise to the global warming problem. The transportations by the automobile, vessel, etc. have largely contributed to the emission of CO_2. Thus, the diesel engines are promising power sources for vehicle because of their high fuel efficiency and low emission of CO_2. Actually, the diesel-powered automobiles have gained widespread use, while nitrogen oxides and particulate matters in the diesel exhaust gas are concerned with the environmental and health problems. Diesel particulate matters mainly consist of soot, and organic compounds of fuel and lubricating oil. The carbonaceous soot particles are removed by diesel particulate filter (DPF). The soot in exhaust gas is trapped and oxidized over a catalyst coated on the DPF [1]. The catalyst is requested to be active for soot combustion at low temperatures because the diesel exhaust gas does not achieve high temperatures.

A number of studies on the catalysts for soot combustion have been carried out extensively so far [2–15]. The CeO_2-based oxides are one of the promising candidate catalysts. The addition of metal oxide to CeO_2 significantly modifies the oxygen storage capacity and surface area. The oxygen storage capacity is associated with the activity in soot combustion since the lattice oxygen in the catalyst directly takes part in this reaction [2]. Moreover, the surface area of catalysts strongly affects the activity of soot oxidation because this reaction proceeds at interface between catalysts and soot. In this study, therefore, we investigated the effect of the additive metal oxides to CeO_2 on their surface area, reduction behavior and catalytic activity for soot oxidation, and then examined the correlation among these properties. Furthermore, the dependence of the amount of additive oxide on the surface area and the catalytic activity was evaluated.

2. Experimental

The catalysts of CeO_2 and MO_x–CeO_2 (M = La, Nd, Mn, Fe, and Cu) were synthesized by the coprecipitation method. The commercial metal nitrates of $Ce(NO_3)_3{\cdot}6H_2O$, $La(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$, $Mn(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ (Wako Pure Chemical Industries) were used as starting materials. A solution of nitrates with an atomic ratio of M/Ce = 1/4 was added dropwise with aqueous ammonia (Wako Pure Chemical Industries) over a period of 1 h to attain a final pH of 10, and stirred for 1 h. After filtration, the obtained precipitate was dried at 120 °C for 6 h and calcined at 650 °C for 5 h. The resultant powder was hereafter abbreviated as M–Ce oxide (cp). The CeO_2–CuO catalysts with various CuO contents (0, 5, 11, 15, and 20 mol%) were also prepared by the citric acid complex method. An aqueous solution of cerium and copper nitrates was stirred at 60 °C for 1 h. Citric acid (Wako Pure Chemical Industries) was added to the solution in a 1.1:1 molar ratio to metal cation, followed by stirring at 60 °C for 2 h. After the evaporation of water at 90 °C, the resulting gel precipitate was heated at 300 °C for 1 h. The obtained powder was calcined at 650 °C for 5 h, and hereafter represented as Cu–Ce oxide (ca).

The crystalline structure of catalysts was analyzed by X-ray diffraction (XRD, Rigaku, Ultima IV X-ray diffractometer). The specific surface area was evaluated by the BET method with N_2

---

* Corresponding author. Tel.: +81 75 383 2519; fax: +81 75 383 2520.
E-mail address: eguchi@scl.kyoto-u.ac.jp (K. Eguchi).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.02.015

Table 1
Specific surface area and catalytic activity in CB oxidation for CeO_2 and M–Ce oxide catalysts.

Sample	Specific surface area ($m^2 g^{-1}$)	T_p (°C)[a]
CB without catalyst	–	725
CeO_2 (cp)	27.3	555
La–Ce oxide (cp)	49.0	535
Nd–Ce oxide (cp)	45.9	569
Mn–Ce oxide (cp)	57.8	475
Fe–Ce oxide (cp)	56.3	480
Cu–Ce oxide (cp)	42.6	472
Cu–Ce oxide (ca)[b]	52.1	430

[a] The peak temperature of the DTG curve in CB oxidation.
[b] Cu content: 11 mol%.

adsorption (BEL Japan, Bellsorp-miniII). The reduction behavior of catalysts was examined by temperature-programmed reduction (TPR, Quantachrome Instruments, CHEMBET 3000). The sample (25 mg) was fixed in a quartz tube reactor, and then a gaseous mixture of 5% H_2/Ar was fed to the reactor at 30 ml min^{-1}. The temperature was raised from room temperature to 950 °C, and the rate of H_2 consumption was measured by a thermal conductivity detector (TCD). To clarify the composition of Cu–Ce oxide (cp) catalyst, Cu content in the filtrate obtained in the preparation stage was determined by measuring the absorbance at 635 nm with UV–vis spectrophotometer (JASCO, V-550).

The catalytic activity for soot combustion was evaluated by thermogravimetric (TG) analysis (Shimadzu, TGA-51). The carbon black (Cabot Inc., V-XC72R, surface area: 224.0 $m^2 g^{-1}$) was used as a model diesel soot. The catalyst and carbon black (CB) were mixed in the weight ratio of 4:1 by grinding with mortar and pestle for 10 min to obtain a tight contact mixture. After pelletizing and pulverizing, the mixed sample (*ca.* 30 mg) was set in the TG apparatus. Prior to the measurement, the sample was heated at 300 °C for 1 h in dry nitrogen to remove the absorbed water, and subsequently cooled and kept at 200 °C under air condition. The TG curve measured at 200–800 °C with a heating rate of 5 °C min^{-1} in air was differentiated, and the peak temperature of the resultant DTG curve was defined as a combustion temperature (T_p). The weight change of the sample was also examined under a dry Ar atmosphere.

3. Results and discussion

When preparing Cu–Ce oxide (cp), copper species could not precipitate completely due to the formation of copper ammonia complex. Then, the composition of resulting catalyst was evaluated by measuring the residual copper species in the solution after filtration. As a result, this catalyst contained 11 mol% CuO. Since the additive metal species readily precipitate as hydroxides for the other M–Ce oxides (cp), these catalysts should attain the desired composition.

The diffraction pattern of all the catalysts corresponded to the cubic CeO_2 phase with fluorite-type structure and no peaks ascribable to the derivates of additive metal components were detected. Thus, the additive species will be highly dispersed as oxides or introduced in CeO_2 structures.

The specific surface area and catalytic activity in CB oxidation for various catalysts are summarized in Table 1. The CB was combusted completely with or without the use of catalysts. The T_p significantly decreased by more than 150 °C in the presence of CeO_2-based catalysts. The addition of metal elements was effective for the enlarged surface area. The catalysts containing rare-earth metal oxides exhibited the analogous activity to CeO_2 (cp). On the contrary, the additive of transition metal oxides enhanced the catalytic activity in CB oxidation. This result agreed well with the previous reports that transition metal oxides added to CeO_2 could significantly promote the oxidation reaction [2,13–15]. In particular, the peak temperature for Cu–Ce oxide (cp) was the lowest of all composite oxides obtained from the coprecipitation method despite the lowest surface area. The reducibility of catalysts was evaluated by TPR analysis to elucidate the oxygen species involved in the CB oxidation, as shown in Fig. 1. It was considered that the reducibility below 650 °C affected the CB oxidation because this reaction completely terminated up to this temperature. For the profile of CeO_2 (cp), two peaks were observed at *ca.* 540 °C and 840 °C, which corresponded to the reduction of surface and bulk of CeO_2, respectively. Below 650 °C, the amount of hydrogen consumption was not changed greatly by the addition of rare-earth metal species. The reduction of La–Ce oxide (cp) started at lower temperature as compared with CeO_2 (cp). Because only the extremely weak peak at *ca.* 620 °C was observed in the profile of La_2O_3 [16], the interaction between Ce and La species may enhance the reducibility of CeO_2. Then, this phenomenon will be responsible for the slight improvement of catalytic activity by the addition of La component. On the other hand, when the transition metal components were added to CeO_2, the large amount of hydrogen consumption was confirmed below 450 °C. These relatively strong peaks were mainly ascribable to the reduction of additive oxides, judging from the reports of TPR analyses for the respective transition metal oxides [16–19]. Interestingly, it was revealed that a part of Ce^{4+} was reduced to Ce^{3+} at 150–300 °C in the Cu–Ce oxide (cp) catalyst because the amount of hydrogen consumption in this temperature range (0.88 mmol $g_{\text{-cat}}{}^{-1}$) was larger than that for the complete reduction from Cu^{2+} to Cu^0 (0.68 mmol $g_{\text{-cat}}{}^{-1}$). This implies that the CeO_2 in the vicinity of CuO can be readily reduced. The reduction behavior of Cu–Ce catalysts did not exhibit a remarkable dependence on the preparation methods. Considering the additive effect of various metal oxides on the surface area, the catalytic activity of CB oxidation, and the reducibility for the catalysts, it can be concluded that the high reducibility at low temperature and the large amount of oxygen species in catalyst available for the oxidation reaction is of primary importance for a superior catalyst. The CB oxidation over CeO_2 (cp) and Cu–Ce oxide (ca) catalysts under an inert atmosphere at 200–600 °C was examined to elucidate the influence of the oxy-

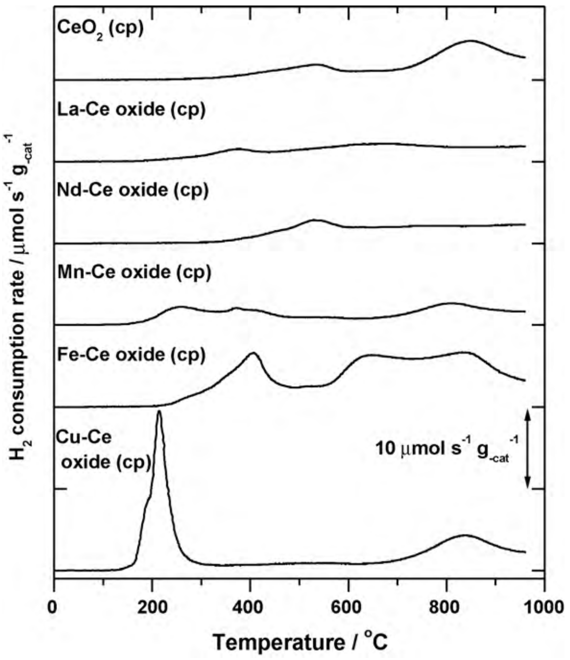

Fig. 1. TPR profiles of CeO_2 (cp) and M–Ce oxide (cp). Reaction conditions: 5% H_2/Ar, total flow rate = 30 ml min^{-1}, heating rate = 10 °C min^{-1}, S.V. = 36,000 l kg^{-1} h^{-1}.

Table 2
Weight loss during CB oxidation over CeO_2 (cp) and Cu–Ce oxide (ca) in dry Ar.

Catalyst	Weight loss (%)
CeO_2 (cp)	0.58
Cu–Ce oxide (ca)[a]	2.85

[a] Cu content: 11 mol%.

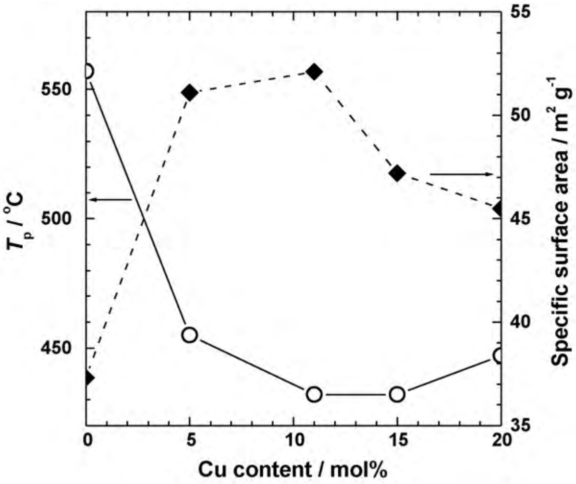

Fig. 2. Specific surface area and T_p for CB oxidation as a function of Cu content for Cu–Ce oxide (ca).

gen species in catalysts on this reaction. As can be seen in Table 2, the CB oxidation proceeded over both catalysts even without oxygen gas. Thus, the oxygen species in the catalysts were consumed for this reaction as reported previously [2]. The weight change was much larger for Cu–Ce oxide (ca) than CeO_2 (cp), suggesting that the available amount of oxygen species in catalyst is strongly associated with the CB oxidation. In addition to this property, the large surface area is a key factor since catalysts and CB are required to contact suitably for the promotion of oxidation reaction by the oxygen species in catalysts. The effect of surface area on the catalytic activity was obvious by comparing the results of Cu–Ce catalysts with the same composition, which were prepared by the different methods: the catalytic activity was increased with an expansion of surface area, though their TPR profiles were quite similar to each other.

For the catalyst of Cu–Ce oxide (ca), which attained the highest activity in CB oxidation of all catalysts investigated, the influence of the additive amount of Cu component on the surface area and catalytic activity was evaluated. Fig. 2 shows the specific surface area and catalytic activity as a function of Cu content for Cu–Ce oxide (ca). The surface area expanded with increasing Cu content up to 11 mol% probably because the interaction of Ce and Cu species should prevent CeO_2 particles from agglomerating during the heat-treatment in the preparation stage. As a result, the addition of Cu species promoted CB oxidation within the CuO content range of 0–11 mol%. This tendency agreed well with the consideration that the contact condition between catalysts and CB plays an important role in the CB oxidation. The further addition of Cu component reduced the catalytic activity. This result originated from the decrease in surface area of catalysts, which should be ascribed to the agglomeration of added CuO particles. Moreover, TPR profiles of Cu–Ce oxide (ca) were recorded to examine the peak mainly attributable to the reduction of CuO. The onset temperature was higher by 20 °C and the hydrogen consumption continued up to higher temperature for 20 mol% Cu–Ce oxide (ca) than 11 mol% Cu–Ce oxide (ca). Accordingly, CuO particles in 11 mol% Cu–Ce oxide (ca) were highly dispersed. These results indicated that the catalytic activity should be dependent on the extent of dispersion of Cu species, which affects the reduction behavior.

4. Conclusions

The soot combustion over the CeO_2-based oxides was investigated, and the additive effect of metal oxides on the surface area, reducibility, and catalytic activity was evaluated. The catalysts were synthesized by the coprecipitation and citric acid complex methods. The CB oxidation was extremely promoted by the use of catalysts due to the oxygen species in catalysts. The activity of catalysts consisting of CeO_2 and rare-earth metal oxide was comparable to that of CeO_2. In contrast, the addition of transition metal oxides greatly contributed to the reduction of CB oxidation temperature. For TPR analysis, the large amount of oxygen species available for the oxidation reaction existed in catalysts containing transition metal oxide at relatively low temperatures. These results indicated that the reduction behavior was associated well with the catalytic CB oxidation. Furthermore, the expansion of catalytic surface area was effective for the reaction because of the improvement of contact condition with CB. The present study clarified that the additive species and preparation method affected the reducibility and surface area of catalysts, giving rise to the difference in the catalytic activity for soot combustion.

References

[1] B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Catal. Rev. Sci. Eng. 43 (2001) 489.
[2] A. Takami, K. Harada, Y. Tsushio, J. Jpn. Petrol. Inst. 50 (2007) 102.
[3] Y. Teraoka, S. Kagawa, Catal. Surv. Jpn. 2 (1998) 155.
[4] Y. Teraoka, K. Kanada, S. Kagawa, Appl. Catal. B: Environ. 34 (2001) 73.
[5] D. Fino, N. Russo, G. Saracco, V. Specchia, J. Catal. 217 (2003) 367.
[6] B. Bialobok, J. Trawczynski, T. Rzadki, W. Mista, M. Zawadzki, Catal. Today 119 (2007) 278.
[7] A. Setiabudi, J. Chen, G. Mul, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 51 (2004) 9.
[8] Q. Liang, X. Wu, X. Wu, D. Weng, Catal. Lett. 119 (2007) 265.
[9] K. Ito, K. Kishikawa, A. Watajima, K. Ikeue, M. Machida, Catal. Commun. 8 (2007) 2176.
[10] T. Masui, K. Minami, K. Koyabu, N. Imanaka, Catal. Today 117 (2006) 187.
[11] K. Krishna, A. Bueno-López, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 75 (2007) 189.
[12] K. Krishna, A. Bueno-López, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 75 (2007) 210.
[13] E. Aneggi, C. de Leitenburg, G. Dolcetti, A. Trovarelli, Catal. Today 114 (2006) 40.
[14] Q. Liang, X. Wu, D. Weng, Z. Lu, Catal. Commun. 9 (2008) 202.
[15] K. Tikhomirov, O. Kröcher, M. Elsener, A. Wokaun, Appl. Catal. B: Environ. 64 (2006) 72.
[16] F.C. Buciuman, F. Patcas, J. Zsakó, J. Therm. Anal. 61 (2000) 819.
[17] F.G. Durán, B.P. Barbero, L.E. Cadús, C. Rojas, M.A. Centeno, J.A. Odriozola, Appl. Catal. B: Environ. 92 (2009) 194.
[18] L.J. Lobree, I.-C. Hwang, J.A. Reimer, A.T. Bell, J. Catal. 186 (1999) 242.
[19] F. Patcas, F.C. Buciuman, J. Zsakó, Thermochim. Acta 360 (2000) 71.